Supporting Information

for

Model Reactions for the Enantioselective Synthesis of γ-Rubromycin: Stereospecific Intramolecular Photoredox Cyclization of an *orhto*-Quinone Ether to a Spiroacetal

Fumihiro Wakita, Yoshio Ando, Ken Ohmori, and Keisuke Suzuki*

Department of Chemistry, Tokyo Institute of Technology 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8551, Japan

E-mail: ksuzuki@chem.titech.ac.jp

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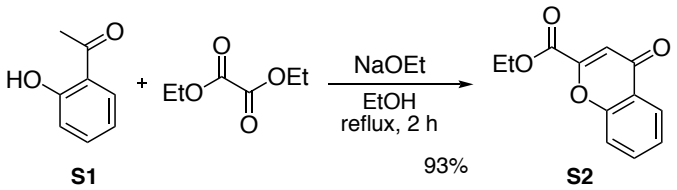
General experimental procedure

All reactions were performed under an argon atmosphere unless otherwise stated. Ethereal solvents and CH_2Cl_2 (anhydrous; *Kanto Chemical Co., Inc.*) were purified under argon by using an Organic Solvent Pure Unit (*Wako Pure Chemical Industries, Ltd.*). DMF, CH_3CN, Et_3N, and *i*-Pr_2NH were distilled prior to use according to the standard protocols. For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (TLC silica gel 60 F_{254}, Art 5715, 0.25 mm) were used. Silica-gel preparative thin-layer chromatography (PTLC) was performed using plates prepared from Merck silica gel 60 PF_{254} (Art 7747). For flash column chromatography, silica gel 60N (Spherical, neutral, 63–210 μm) from Kanto Chemical was used. Melting point (mp) determinations were performed using a Yanaco MP-500 instrument or a METTLER TOLEDO MP 70 melting point system, and are uncorrected. ^{1}H- and ^{13}C-NMR were measured on a Bruker Avance III 600 (600 MHz) spectrometer in the solvent indicated; Chemical shifts (δ) are expressed in parts per million (ppm) downfield from internal standard (tetramethylsilane, 0.00 ppm or 7.26 ppm for $CDCl_3$, and 2.04 ppm for acetone-d_6), and coupling constants (*J*) are reported as hertz (Hz). Splitting patterns are indicated as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad. Infrared (IR) spectra were recorded on a Thermo Fisher SCIENTIFIC NICOLET iS5 FTIR spectrometer. Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra were recorded by using a Thermo Fisher SCIENTIFIC NICOLET iS5 FTIR spectrometer. High-resolution mass spectra (HRMS) were obtained with a Bruker micrOTOF–QII (ESI or APCI). High performance liquid chromatography (HPLC) analyses were performed by a LC-NetII/ADC for controller, a PU-2086 Plus for HPLC pump, and a UV-2075 Plus for UV/Vis detector. Photoreaction was performed using ASAHI SPECTRA Xenon Light Source MAX–303 (VIS). UV–VIS spectrum was recorded by using a JASCO V-650 spectrometer. X-ray crystallographic data was recorded with a RIGAKU R-AXIS RAPID-II IP diffractometer.

benzopyranone **S2**

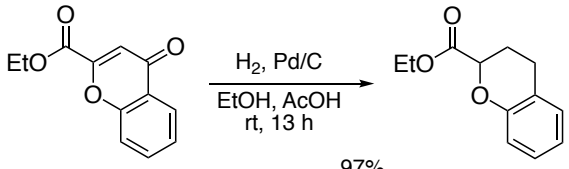


S1 **S2**

To a solution of **S1** (2.60 mL, 21.6 mmol) and diethyl oxalate (7.8 mL, 58 mmol) in EtOH (320 mL) was added NaOEt (7.6 g, 112 mmol) at room temperature. The reaction was refluxed for 2 h. After cooling to room temperature, the mixture was concentrated in vacuo. The residue was diluted with water and quenched by adding saturated aqueous NH_4Cl at 0 °C. The mixture was extracted with CH_2Cl_2 (×3). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 3/1) to afford benzopyranone **S2** (4.38 g, 93%) as a yellow solid. Spectroscopic data were identical with reported data.[1]

benzopyranone **S2**: R_f 0.38 (hexane/EtOAc = 3/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.42 (t, 3H, J = 7.1 Hz), 4.47 (q, 2H, J = 7.1 Hz), 7.13 (s, 1H), 7.46 (ddd, 1H, J = 8.0, 7.1, 1.1 Hz), 7.62 (dd, 1H, J = 8.7, 1.1 Hz), 7.75 (ddd, 1H, J = 8.7, 7.1, 1.8 Hz), 8.21 (dd, 1H, J = 8.0, 1.8 Hz).

chromane **S3**

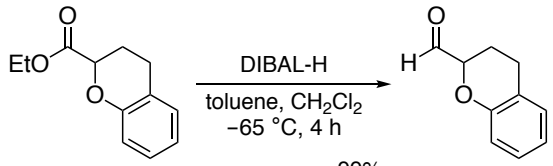


S2 **S3**

A flask, thoroughly purged with argon, was charged with 10% Pd/C (1.17 g), to which was added a solution of benzopyranone **S2** (4.38 g, 20.1 mmol) in EtOH (120 mL) and AcOH (14 mL). The atmosphere was changed from argon to H_2 (1 atm), and the mixture was vigorously stirred for 13 h at room temperature. After changing the atmosphere from H_2 to argon, the mixture was filtered through a Celite® pad (rinsed with EtOAc) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 5/1) to afford chromane **S3** (3.89 g, 94%) as a pale yellow oil. Spectroscopic data were identical with reported data.[2]

chromane **S3**: R_f 0.55 (hexane/EtOAc = 3/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.29 (t, 3H, J = 7.1 Hz), 2.14–2.22 (m, 1H), 2.22–2.33 (m, 1H), 2.70–2.80 (m, 1H), 2.80–2.90 (m, 1H), 4.26 (q, 2H, J = 7.1 Hz), 4.71 (dd, 1H, J = 7.6, 4.1 Hz), 6.87 (dd, 1H, J = 7.8, 7.2 Hz), 6.93 (d, 1H, J = 7.8 Hz), 7.03 (d, 1H, J = 7.2 Hz), 7.11 (dd, 1H, J = 7.8, 7.2 Hz).

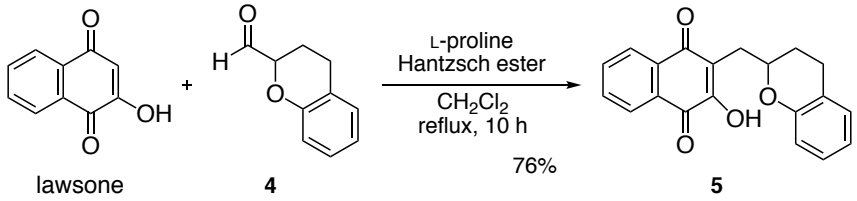
aldehyde **4**



To a solution of **S3** (1.10 g, 5.32 mmol) in toluene (8.0 mL) and CH_2Cl_2 (2.0 mL) was added DIBAL-H (0.61 M solution in hexane, 9.2 mL, 5.6 mmol) at –65 °C. After stiring for 4 h at –65 °C, the reaction was stopped by adding MeOH (8.0 mL) at –65 °C and allowed to warm to room temperature. The mixture was filtered through a Celite® pad (rinsed with CH_2Cl_2) and washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 2/1) to afford aldehyde **4** (852 mg, 99%) as a pale yellow oil. Spectroscopic data were identical with reported data.[2]

aldehyde **4**: R_f 0.43 (hexane/EtOAc = 3/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.98–2.28 (m, 2H), 2.68–2.91 (m, 2H), 4.49 (ddd, 1H, J = 8.7, 3.5, 0.7 Hz), 6.80–6.95 (m, 2H), 7.06–7.17 (m, 2H), 9.83 (s, 1H).

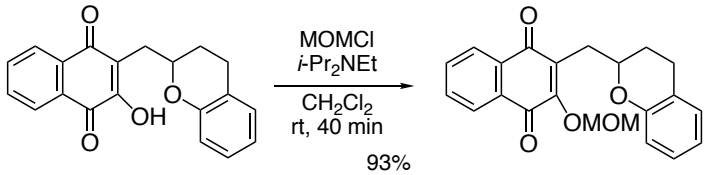
hydroxynaphthoquinone **5**



To a solution of **4** (335 mg, 2.07 mmol) in CH_2Cl_2 (40 mL) was added lawsone (641 mg, 3.68 mmol), L-proline (121 mg, 1.05 mmol) and Hantzsch ester (551 mg, 2.18 mmol) at room temperature. The reaction was refluxed for 10 h. After cooling to room temperature, the mixture was concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 6/1) to afford hydroxynaphthoquinone **5** (500 mg, 76%) as an orange solid.

hydroxynaphthoquinone **5** (racemic): R_f 0.28 (hexane/EtOAc = 3/1); mp 145–147°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.80–1.88 (m, 1H), 2.02–2.08 (m, 1H), 2.77–2.85 (m, 2H), 2.97 (dd, 1H, J = 13.2, 6.0 Hz), 3.13 (dd, 1H, J = 13.2, 7.2 Hz), 4.34–4.39 (m, 1H), 6.75 (d, 1H, J = 7.8 Hz), 6.81 (t, 1H, J = 7.2 Hz), 7.02 (d, 1H, J = 7.2 Hz), 7.05 (t, 1H, J = 7.8 Hz), 7.55 (br-s, 1H, OH), 7.70 (dd, 1H, J = 7.8, 7.2 Hz), 7.77 (dd, 1H, J = 7.8, 7.2 Hz), 8.11 (d, 1H, J = 7.2 Hz), 8.15 (d, 1H, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.4, 27.3, 29.3, 74.4, 116.8, 120.13, 120.19, 121.8, 126.2, 126.9, 127.1, 129.4, 129.5, 132.8, 133.0, 135.0, 154.4, 154.5, 181.2, 184.5; IR (neat) 3343, 1669, 1634, 1592, 1587, 1494, 1458, 1340, 1273, 1229, 1073, 1048, 999, 725, 676 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{17}O_4$ ($[M+H]^+$) m/z 321.1121, found m/z 321.1118.

naphthoquinone **6**

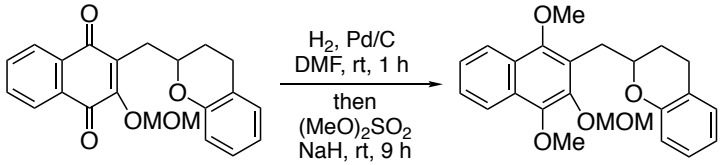


5 **6**

To a solution of **5** (238 mg, 0.742 mmol) in CH_2Cl_2 (3.7 mL) was added *i*-Pr_2NEt (260 μL, 1.48 mmol) and MOMCl (90 μL, 1.2 mmol) at room temperature. After stirring for 40 min, the reaction was quenched by adding saturated aqueous $NaHCO_3$ at 0 °C. The mixture was extracted with CH_2Cl_2 (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 5/1) to afford naphthoquinone **6** (253 mg, 93%) as a yellow oil.

naphthoquinone **6**: R_f 0.46 (hexane/EtOAc = 5/1); ^{1}H NMR (600 MHz, acetone-d_6) δ 1.73–1.81 (m, 1H), 2.08–2.13 (m, 1H), 2.73–2.82 (m, 2H), 3.00 (dd, 1H, *J* = 12.6, 7.2 Hz), 3.18 (dd, 1H, *J* = 12.6, 6.9 Hz), 3.54 (s, 3H), 4.33–4.38 (m, 1H), 5.51 (d, 1H, *J* = 5.4 Hz), 5.54 (d, 1H, *J* = 5.4 Hz), 6.98 (d, 1H, *J* = 7.8 Hz), 6.75–6.79 (m, 1H), 6.99–7.04 (m, 2H), 7.82–7.87 (m, 2H), 8.05–8.08 (m, 2H); ^{13}C NMR (150 MHz, acetone-d_6) δ 25.0, 28.1, 30.5, 57.8, 75.4, 99.6, 117.4, 120.8, 122.9, 126.8, 126.9, 127.8, 130.3, 132.2, 132.5, 132.9, 134.4, 135.0, 155.7, 157.9, 182.1, 185.7; IR (ATR) 3018, 2930, 2848, 1670, 1610, 1581, 1488, 1457, 1340, 1296, 1231, 1159, 1073, 950, 903, 756, 726, 667 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{20}O_5Na$ ([M+Na]$^+$) *m/z* 387.1203, found *m/z* 387.1209.

naphthalene **7**

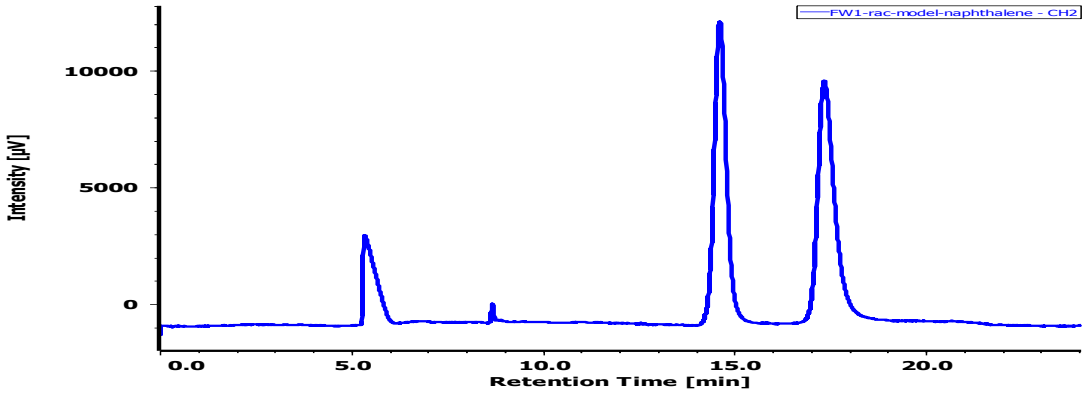


6 **7**

A flask, thoroughly purged with argon, was charged with 10% Pd/C (7.8 mg), to which was added a solution of naphthoquinone **6** (61.4 mg, 0.168 mmol) in DMF (1.1 mL) at room temperature. The atmosphere was changed from argon to H_2 (1 atm), and the mixture was vigorously stirred for 1 h at room temperature. After changing the atmosphere from H_2 to argon, the mixture was added NaH (63% dispersion in oil, 25.7 mg, 0.674 mmol) and $(MeO)_2SO_2$ (32 μL, 0.34 mmol). The atmosphere was changed from argon to H_2 (1 atm), and the mixture was vigorously stirred for 9 h at room temperature. After changing the atmosphere from H_2 to argon, the mixture was stopped by adding diethylamine (174 μL, 1.68 mmol) and water at 0 °C and filtered through a Celite® pad (rinsed with EtOAc). The mixture was extracted with EtOAc (×3), and the combined organic extracts were washed with saturated aqueous NH_4Cl, and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by PTLC (silica gel, hexane/EtOAc = 4/1) to afford naphthalene **7** (60.3 mg, 91%) as a pale yellow oil. Racemic mixture of **7** were separated by preparative HPLC on a chiral stationary phase [DAICEL CHIRALPAK® IF (2 cm φ × 25 cm), UV detection at 254 nm, hexane/*i*-PrOH = 99/1, flow rate 8.0 mL/min] to give (*S*)-7 (t_R = 32.2 min)

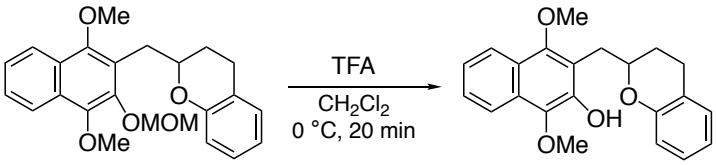
as a pale yellow oil and (*R*)-7 (t_R = 38.2 min) as a pale yellow oil.

Enantiomeric purity of **7** was assessed by HPLC analysis on a chiral stationary phase [DAICEL CHIRALPAK® IF (0.46 cm φ × 25 cm), UV detection at 254 nm, hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, t_R =14.5 min for (*S*)-isomer and 17.1 min for (*R*)-isomer.]



naphthalene **7**: R_f 0.49 (hexane/EtOAc = 5/1); (*S*)-**7**, t_R = 14.5 min, $[\alpha]_D^{20}$ +45 (*c* 0.92, $CHCl_3$); (*R*)-**7**, t_R = 17.1 min $[\alpha]_D^{20}$ –49 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.81–1.89 (m, 1H), 1.95–2.01 (m, 1H), 2.75–2.80 (m, 2H), 3.19 (dd, 1H, *J* = 13.2, 7.8 Hz), 3.43 (dd, 1H, *J* = 13.2, 6.0 Hz), 3.62 (s, 3H), 3.94 (s, 3H), 3.97 (s, 3H), 4.44–4.50 (m, 1H), 5.29 (d, 1H, *J* = 5.7 Hz), 5.33 (d, 1H, *J* = 5.7 Hz), 6.77 (d, 1H, *J* = 7.8 Hz), 6.81 (t, 1H, *J* = 7.2 Hz), 7.03 (d, 1H, *J* = 7.8 Hz), 7.06 (dd, 1H, *J* = 8.4, 7.2 Hz), 7.44–7.51 (m, 2H), 8.03 (d, 1H, *J* = 7.8 Hz), 8.09 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.8, 27.0, 31.3, 57.7, 61.0, 62.3, 75.7, 99.6, 116.7, 119.9, 121.7, 122.25, 122.34, 123.4, 125.1, 125.6, 126.0, 127.0, 128.5, 129.5, 143.2, 146.1, 151.3, 155.1; IR (ATR) 2935, 2844, 1582, 1488, 1457, 1361, 1358, 1238, 1160, 1070, 1040 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{26}O_5Na$ ($[M+Na]^+$) *m/z* 417.1673, found *m/z* 417.1674.

phenol **8**

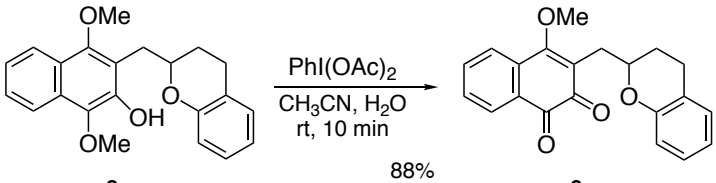


To a solution of **7** (236 mg, 0.598 mmol) in CH_2Cl_2 (3.0 mL) was added TFA (0.6 mL) at 0 °C. After stirring for 20 min, the reaction was quenched by adding saturated aqueous $NaHCO_3$ at 0 °C. The mixture was extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (silica gel, hexane/EtOAc = 2/1) to afford phenol **8** (192 mg, 92%) as a pale yellow solid.

According to the same procedure, (*R*)-**7** and (*S*)-**7** were converted to (*R*)-**8** and (*S*)-**8**, respectively.

phenol **8**: R_f 0.39 (hexane/EtOAc = 5/1); (*S*)-**8**, $[\alpha]_D^{20}$ +21 (*c* 1.05, $CHCl_3$); (*R*)-**8**, $[\alpha]_D^{20}$ –21 (*c* 0.99, $CHCl_3$); mp 110–111°C (racemic); ^{1}H NMR (600 MHz, acetone-d_6) δ 1.74–1.83 (m, 1H), 1.97–2.03 (m, 1H), 2.75–2.79 (m, 2H), 3.18 (dd, 1H, *J* = 13.2, 7.8 Hz), 3.37 (dd, 1H, *J* = 13.2, 6.6 Hz), 3.88 (s, 3H), 3.96 (s, 3H), 4.45–4.51 (m, 1H), 6.71 (d, 1H, *J* = 7.8 Hz), 6.77 (t, 1H, *J* = 7.2 Hz), 7.00–7.04 (m, 2H), 7.36 (dd, 1H, *J* = 7.8, 7.2 Hz), 7.47 (dd, 1H, *J* = 7.8, 7.2 Hz), 7.95 (d, 1H, *J* = 8.4 Hz), 8.01 (d, 1H, *J* = 8.4 Hz), 8.34 (s, 1H, OH); ^{13}C NMR (150 MHz, acetone-d_6) δ 25.3, 27.9, 31.6, 61.7, 62.7, 76.2, 117.3, 120.1, 120.7, 121.4, 123.1, 123.4, 123.9, 124.1, 126.9, 127.8, 128.9, 130.4, 137.7, 146.6, 152.6, 155.9; IR (neat) 3364, 2952, 1624, 1598, 1582, 1487, 1458, 1365, 1276, 1226, 1192, 1067, 1037, 969, 770, 735 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{23}O_4$ ($[M+H]^+$) *m/z* 351.1591, found *m/z* 351.1592.

naphthoquinone **9**



8 **9**

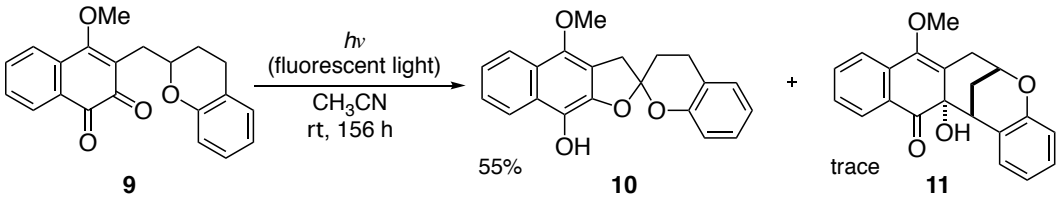
To a solution of naphthalene **8** (22.3 mg, 0.0636 mmol) in CH_3CN (1.3 mL) and water (0.40 mL) was added diacetoxyiodobenzene (24.6 mg, 0.0764 mmol) at room temperature. After stirring for 10 min, the reaction was quenched by saturated aqueous $NaHCO_3$ at 0 °C and poured into a mixed solvent of water and EtOAc. The mixture was extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by PTLC (silica gel, hexane/EtOAc = 3/2) to afford naphthoquinone **9** (18.7 mg, 88%) as an orange solid.

According to the same procedure, (*R*)-**8** and (*S*)-**8** were converted to (*R*)-**9** and (*S*)-**9**, respectively.

naphthoquinone **9**: R_f 0.40 (hexane/EtOAc = 3/1); (*S*)-**9**, $[\alpha]_D^{20}$ –127 (*c* 0.82, $CHCl_3$); (*R*)-**9**, $[\alpha]_D^{20}$ +114 (*c* 0.78, $CHCl_3$); mp 126–128 °C (racemic); ^{1}H NMR (600 MHz, acetone-d_6) δ 1.70–1.77 (m, 1H), 2.09–2.15 (m, 1H), 2.77–2.85 (m, 2H), 2.84 (dd, 1H, *J* = 13.2, 6.6 Hz), 3.02 (dd, 1H, *J* = 13.2, 7.2 Hz), 4.11 (s, 3H), 4.23–4.28 (m, 1H), 6.68 (d, 1H, *J* = 7.8 Hz), 6.75–6.79 (m, 1H), 7.01 (dd, 1H, *J* = 7.2, 6.6 Hz), 7.02 (d, 1H, *J* = 7.2 Hz), 7.60–7.64 (m, 1H), 7.78–7.84 (m, 2H), 8.01 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, acetone-d_6) δ 25.2, 28.2, 30.7, 62.6, 75.1, 117.3, 120.8, 122.9, 126.2, 126.3, 127.8, 129.6, 130.4, 131.5, 131.6, 133.4, 136.2, 155.7, 167.9, 179.4, 182.2; IR (neat) 2943, 2838, 1692, 1652, 1608, 1582, 1488, 1455, 1349, 1273, 1230, 1219, 1116, 1088, 1061, 961, 885, 785, 759, 735, 705 cm^{-1}; UV–Vis (CH_3CN) λ_{max} nm (ε) = 415 (1652), 331 (1512), 254 (21916); HRMS (ESI-TOF) calcd for $C_{21}H_{19}O_4$ ($[M+H]^+$) *m/z* 335.1278, found *m/z* 335.1271.

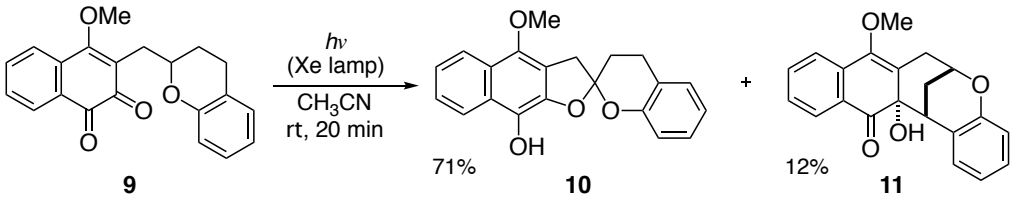
spiroacetal **10**

fluorescent light irradiation



To a solution of naphthoquinone **9** (27.3 mg, 0.0816 mmol) in CH_3CN (8.1 mL) was placed in a Pyrex® two necked round bottomed flask, and degassed three times by purging with argon under sonication. The solution was irradiated by visible light (Panasonic FHF32EX-D-H, 32W; distance from flask: ca. 1 m) for 156 h at room temperature. The reaction was concentrated in vacuo. The residue was purified by column PTLC (silica gel, hexane/EtOAc = 3/2) to afford spiroacetal **10** (14.7 mg, 55%) as a white solid, naphthoquinone **9** (2.5 mg, 9%) as an orange solid, and trace amount of alcohol **11**.

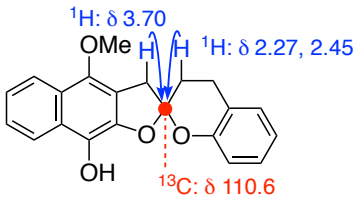
xenon lamp irradiation



To a solution of naphthoquinone **9** (19.1 mg, 0.0577 mmol) in CH_3CN (5.8 mL) was placed in a pyrex® two necked round bottomed flask, and degassed three times by purging with argon under sonication. The solution was irradiated by visible light (asahi spectra 300 W xenon lamp, >380 nm) for 20 min at room temperature. The reaction was concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 6/1) to afford spiroacetal **10** (13.7 mg, 71%) as a white solid, alcohol **11** (2.3 mg, 12%) as a pale yellow solid, and naphthoquinone **9** (1.5 mg, 8%) as an orange solid.

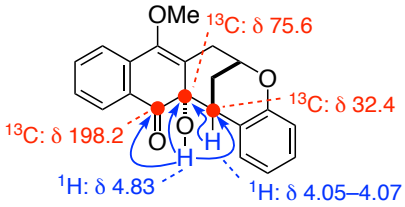
spiroacetal **10** (racemic): R_f 0.48 (hexane/EtOAc = 3/1); mp 153 °C (decomp.); ^{1}H NMR (600 MHz, acetone-d_6) δ 2.27 (td, 1H, J = 13.2, 5.4 Hz), 2.45 (ddd, 1H, J = 13.2, 5.7, 2.1 Hz), 2.83–2.89 (m, 1H), 3.14–3.22 (m, 1H), 3.70 (s, 2H), 4.01 (s, 3H), 6.72 (d, 1H, J = 7.8 Hz), 6.95 (t, 1H, J = 7.2 Hz), 7.13 (dd, 1H, J = 7.8, 7.2 Hz), 7.18 (d, 1H, J = 7.2 Hz), 7.33 (dd, 1H, J = 7.8, 7.2 Hz), 7.40 (dd, 1H, J = 8.4, 7.2 Hz), 8.02 (d, 1H, J = 8.4 Hz), 8.09 (d, 1H, J = 7.8 Hz), 8.36 (s, 1H, OH); ^{13}C NMR (150 MHz, acetone-d_6) δ 22.4, 30.7, 41.3, 60.6, 110.6, 116.8, 117.7, 122.01, 122.02, 122.4, 122.8, 124.0, 125.1, 125.7, 127.7, 128.3, 130.1, 130.2, 142.0, 145.4, 153.4; IR (neat) 3380, 2924, 1650, 1642, 1585, 1492, 1433, 1379, 1310, 1206, 1175, 1093, 982, 955, 917, 832, 751, 636 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{19}O_4$ ($[M+H]^+$) *m/z* 335.1278, found *m/z* 335.1272.

Key HMBC Correlations



alcohol **11** (racemic): R_f 0.38 (hexane/EtOAc = 3/1); mp 149–151 °C; ^{1}H NMR (600 MHz, acetone-d_6) δ 1.45 (dt, 1H, J = 13.8, 2.4 Hz), 1.85 (dt, 1H, J = 13.8, 3.0 Hz), 2.29 (dd, 1H, J = 16.2, 3.0 Hz), 3.59 (dd, 1H, J = 16.2, 8.4 Hz), 3.72 (s, 3H), 4.05–4.07 (m, 1H), 4.83 (brs, 1H, OH), 4.87 (dtd, 1H, J = 9.6, 3.0, 2.4 Hz), 6.78 (d, 1H, J = 7.8 Hz), 6.83 (td, 1H, J = 7.2, 0.6 Hz), 7.16 (td, 1H, J = 7.2, 1.2 Hz), 7.22 (dd, 1H, J = 7.8, 0.6 Hz), 7.45 (td, 1H, J = 7.8, 0.6 Hz), 7.49 (d, 1H, J = 7.8 Hz), 7.67 (td, 1H, J = 7.8, 1.2 Hz), 7.90 (td, 1H, J = 7.8, 1.2 Hz); ^{13}C NMR (150 MHz, acetone-d_6) δ 26.7, 28.6, 32.4, 61.0, 69.7, 75.6, 117.9, 120.0, 123.2, 123.6, 125.1, 128.3, 128.8, 129.3, 130.0, 134.8, 135.1, 135.5, 151.5, 153.5, 198.2; IR (neat) 3413, 2951, 2928, 2851, 1703, 1597, 1582, 1485, 1454, 1272, 1218, 1078, 1048, 1009, 958, 757, 718, 683 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{18}O_4Na$ ([M+Na]$^+$) *m/z* 357.1097, found *m/z* 357.1093.

Key HMBC Correlations



Key NOE Correlation

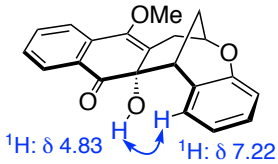
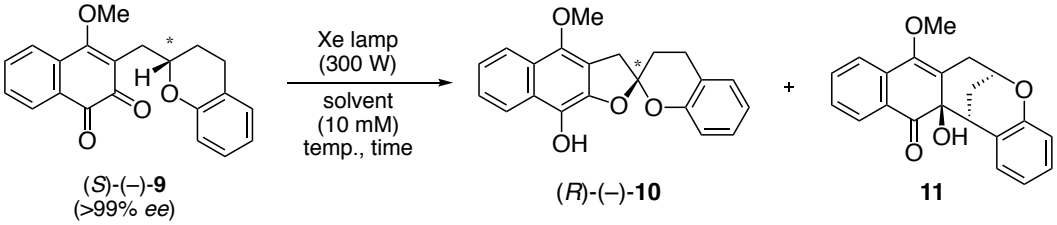


Table S-1. Optimization of photoredox reaction of (*S*)-(–)-**9**.



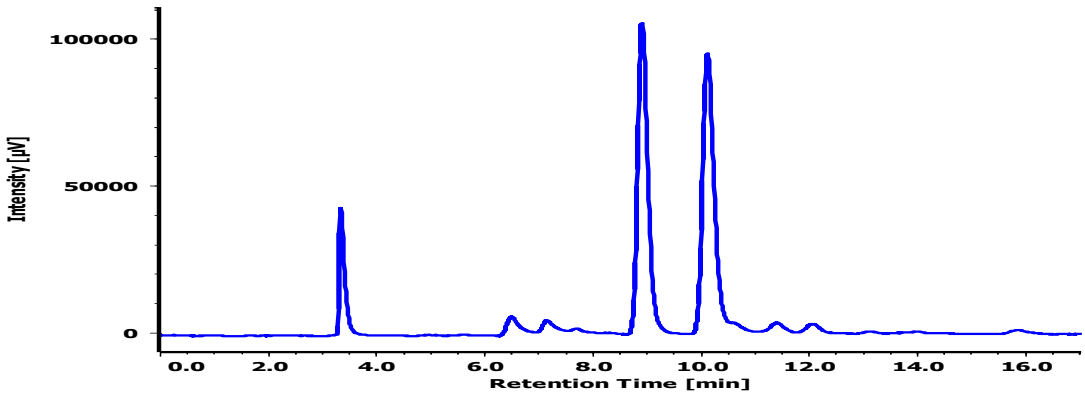
(*S*)-(–)-**9** (>99% *ee*) | (*R*)-(–)-**10** | **11**

entry	solvent	temp. / °C	time	**10** / %	% *ee*	**11** / %	**9** (recovery) / %
1	CH_3CN	rt	20 min	69	53	18	7
2	toluene	rt	20 min	10	12	5	16
3	THF	rt	20 min	33	13	–	18
4	acetone	rt	20 min	34	42	5	29
5	CH_2Cl_2	rt	20 min	46	31	16	–
6	MeOH	rt	20 min	64	77	10	7
7	EtOH	rt	20 min	51	61	21	6
8	*i*-PrOH	rt	20 min	44	45	11	10
9	MeOH	0	70 min	65	82	9	5
10	MeOH	–40	2 h	70	87	10	8
11	MeOH	–78	3 h	34	98	–	39
12	MeOH, CH_3CN (3 / 1)	–78	3 h	68	98	–	13

Enantiomeric purity of (*R*)-**10** was assessed by HPLC analysis on a chiral stationary phase [DAICEL CHIRALPAK® IB (0.46 cm φ × 25 cm), UV detection at 254 nm, hexane/EtOAc= 85/15, flow rate 1.0 mL/min, t_R = 8.9 min for (*R*)-isomer, and 10.1 min for (*S*)-isomer]

Each HPLC analyses in Table S-1 are shown as follows. Some chromatograms contain a few impurities due to lability of **10**.

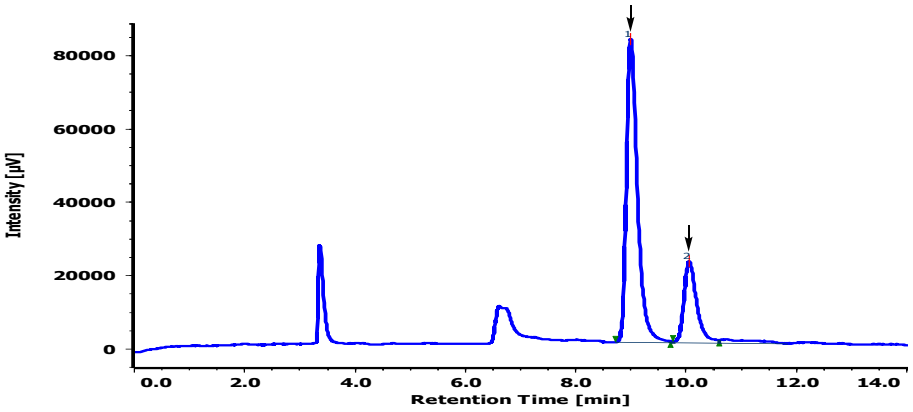
Recemic material of spiroacetal **10**



entry 1 (CH_3CN, rt, 53% *ee*)

To a solution of naphthoquinone (*S*)-**9** (18.8 mg, 0.0562 mmol) in CH_3CN (5.6 mL) was placed in a Pyrex® two necked round bottomed flask, and degassed three times by purging with argon under sonication. The solution was

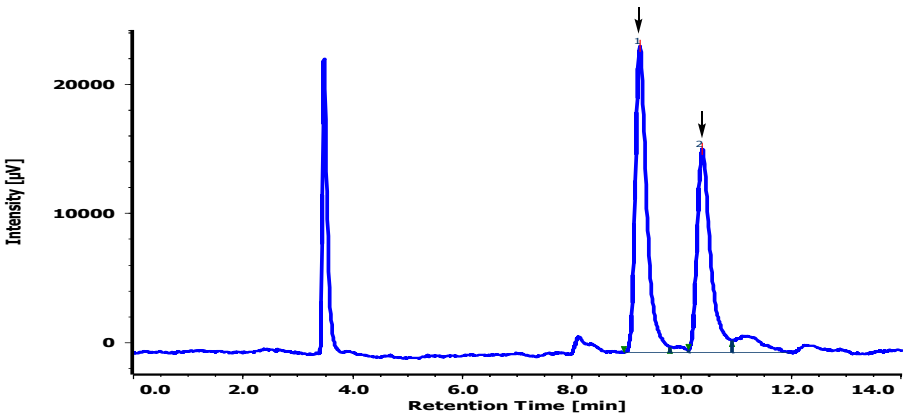
irradiated by visible light (asahi spectra 300 W xenon lamp, >380 nm) for 20 min at room temperature. The reaction was concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 6/1) to afford spiroacetal (*R*)-**10** (12.9 mg, 69%, 53% *ee*) as a white solid, alcohol **11** (3.4 mg, 18%) as a pale yellow solid, and naphthoquinone (*S*)-**9** (1.3 mg, 7%) as an orange solid.



	tR/min	peak area	peak area%
(*R*)-**10**	8.983	1152907	76.299
(*S*)-**10**	10.042	358132	23.701

entry 2 (toluene, rt, 12% *ee*)

According to the synthesis of (*R*)-**10**, 1,2-quinone (*S*)-**9** (6.4 mg, 0.019 mmol) in tolulene (1.9 mL) was irradiated for 20 min at room temperature and resulted crude material was purified by PTLC (silica gel, hexane/EtOAc = 2/1) to afford (*R*)-**10** (0.6 mg, 10%, 12% *ee*) as a while solid, **11** (0.3 mg, 5%) as a pale yellow solid, and (*S*)-**9** (1.0 mg, 16%) as a orange solid.

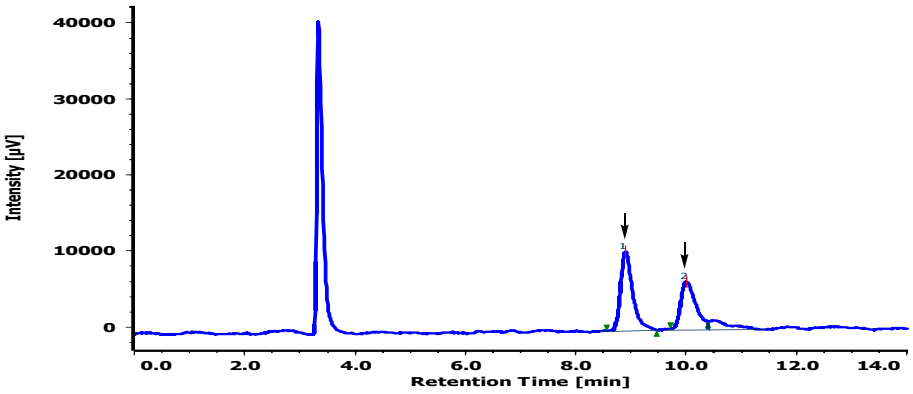


	tR/min	peak area	peak area%
(*R*)-**10**	9.225	344540	55.922
(*S*)-**10**	10.367	271567	44.078

entry 3 (THF, rt, 13% *ee*)

According to the synthesis of (*R*)-**10**, 1,2-quinone (*S*)-**9** (6.0 mg, 0.018 mmol) in THF (1.8 mL) was irradiated for

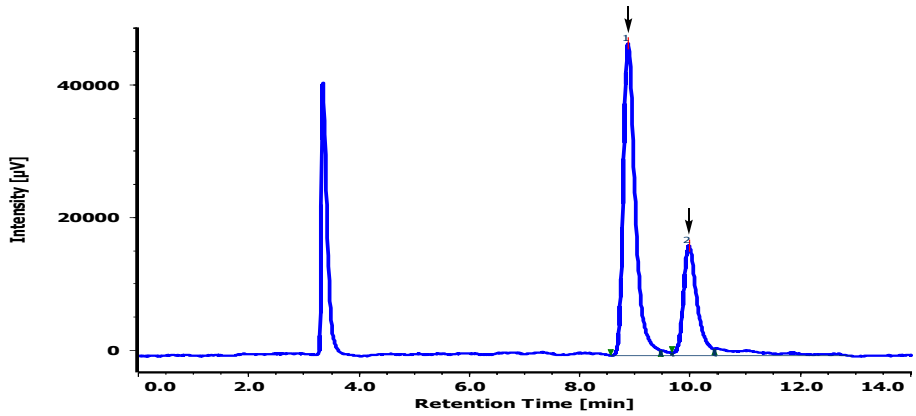
20 min at room temperature and resulted crude material was purified by PTLC (silica gel, hexane/EtOAc = 3/2) to afford (*R*)-**10** (2.0 mg, 33%, 13% *ee*) as a while solid and (*S*)-**9** (1.1 mg, 18%) as a orange solid.



	tR/min	peak area	peak area%
(*R*)-**10**	8.883	158157	56.667
(*S*)-**10**	9.992	120944	43.333

entry 4 (acetone, rt, 42% *ee*)

According to the synthesis of (*R*)-**10**, 1,2-quinone (*S*)-**9** (6.1 mg, 0.018 mmol) in acetone (1.8 mL) was irradiated for 20 min at room temperature and resulted crude material was purified by PTLC (silica gel, hexane/EtOAc = 3/2) to afford (*R*)-**10** (2.1 mg, 34%, 42% *ee*) as a while solid, **11** (0.3 mg, 5%) as a pale yellow solid, and (*S*)-**9** (1.8 mg, 29%) as a orange solid.

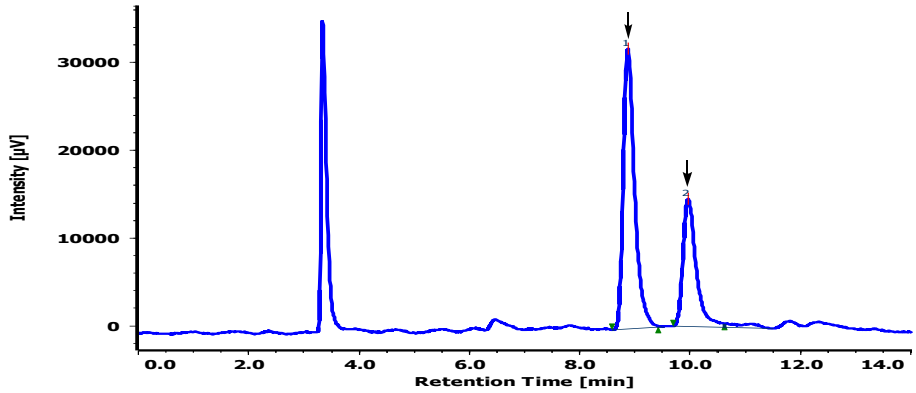


	tR/min	peak area	peak area%
(*R*)-**10**	8.867	709241	71.204
(*S*)-**10**	9.967	286832	28.796

entry 5 (CH_2Cl_2, rt, 31% *ee*)

According to the synthesis of (*R*)-**10**, 1,2-quinone (*S*)-**9** (6.3 mg, 0.019 mmol) in CH_2Cl_2 (1.9 mL) was irradiated for 20 min at room temperature and resulted crude material was purified by PTLC (silica gel, hexane/EtOAc =

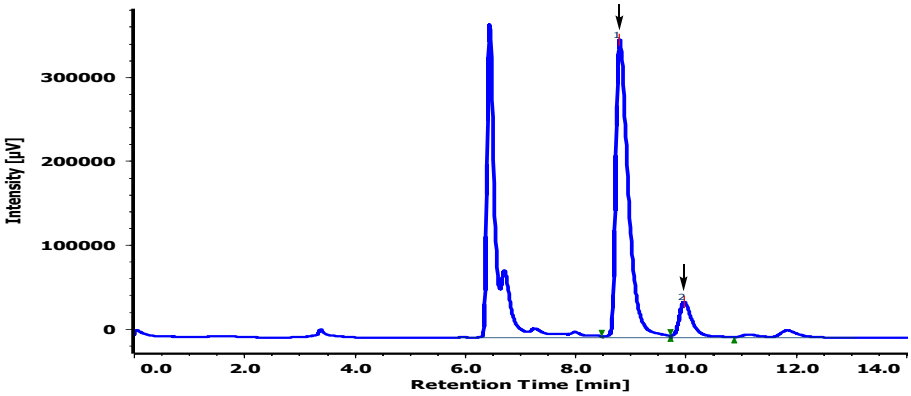
3/2) to afford (*R*)-**10** (2.9 mg, 46%, 31% *ee*) as a while solid and **11** (1.0 mg, 16%) as a pale yellow solid.



	tR/min	peak area	peak area%
(*R*)-**10**	8.858	455817	65.274
(*S*)-**10**	9.942	242498	34.726

entry 6 (MeOH, rt, 77% *ee*)

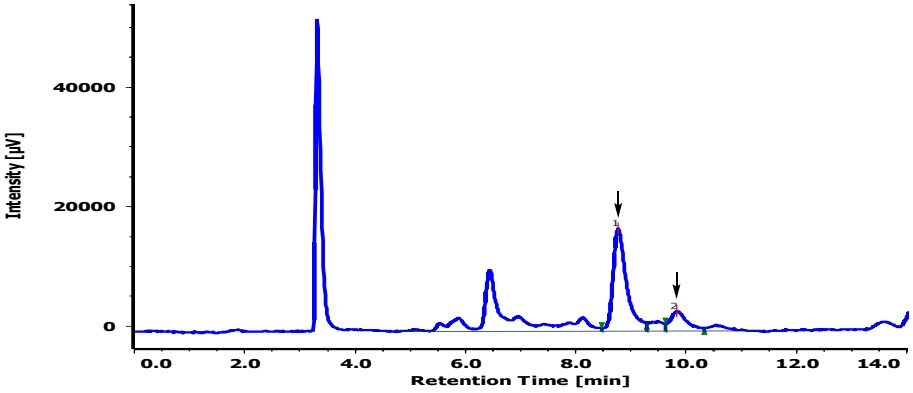
According to the synthesis of (*R*)-**10**, 1,2-quinone (*S*)-**9** (5.8 mg, 0.017 mmol) in MeOH (1.7 mL) was irradiated for 20 min at room temperature and resulted crude material was purified by column chromatography (silica gel, hexane/EtOAc = 6/1) to afford (*R*)-**10** (3.7 mg, 64%, 77% *ee*) as a while solid, **11** (0.6 mg, 10%) as a pale yellow solid, and (*S*)-**9** (0.4 mg, 7%) as a orange solid.



	tR/min	peak area	peak area%
(*R*)-**10**	8.783	5609841	88.437
(*S*)-**10**	9.950	733450	11.563

entry 7 (EtOH, rt, 61% *ee*)

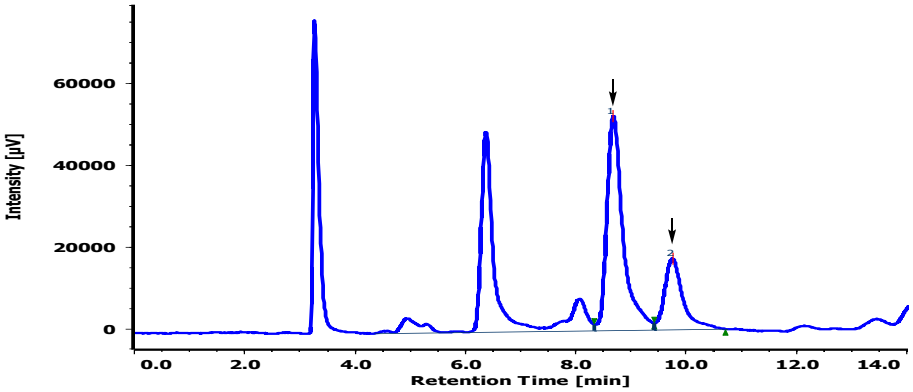
According to the synthesis of (*R*)-**10**, 1,2-quinone (*S*)-**9** (14.9 mg, 0.0446 mmol) in EtOH (4.5 mL) was irradiated for 20 min at room temperature and resulted crude material was purified by column chromatography (silica gel, hexane/EtOAc = 6/1) to afford (*R*)-**10** (7.6 mg, 51%, 61% *ee*) as a while solid, **11** (3.1 mg, 21%) as a pale yellow solid, and (*S*)-**9** (1.0 mg, 7%) as a orange solid.



	tR/min	peak area	peak area%
(*R*)-**10**	8.750	296476	80.565
(*S*)-**10**	9.817	71519	19.435

entry 8 (*i*-PrOH, rt, 45% *ee*)

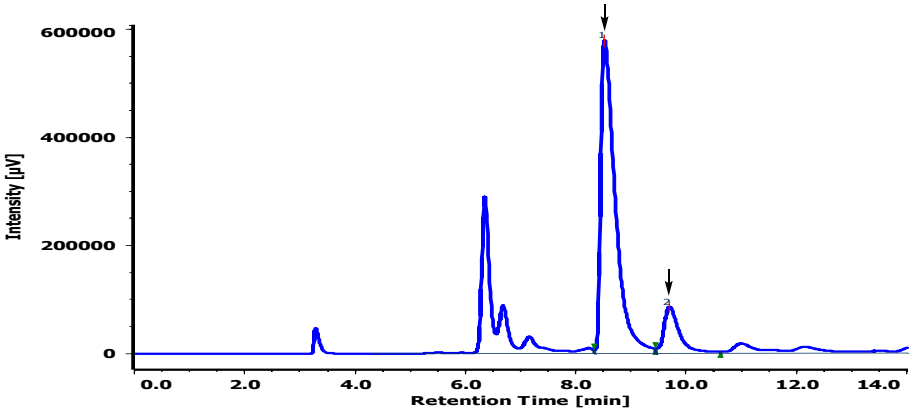
According to the synthesis of (*R*)-**10**, 1,2-quinone (*S*)-**9** (14.8 mg, 0.0443 mmol) in *i*-PrOH (4.4 mL) was irradiated for 20 min at room temperature and resulted crude material was purified by column chromatography (silica gel, hexane/EtOAc = 6/1) to afford (*R*)-**10** (6.5 mg, 44%, 45% *ee*) as a while solid, **11** (1.6 mg, 11%) as a pale yellow solid, and (*S*)-**9** (1.5 mg, 10%) as a orange solid.



	tR/min	peak area	peak area%
(*R*)-**10**	8.667	1072964	72.564
(*S*)-**10**	9.742	405680	27.436

entry 9 (MeOH, 0 °C, 82% *ee*)

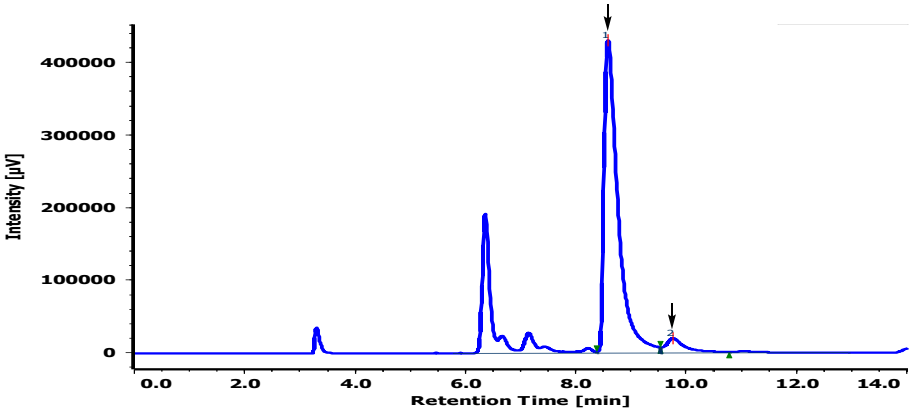
According to the synthesis of (*R*)-**10**, 1,2-quinone (*S*)-**9** (17.3 mg, 0.0517 mmol) in MeOH (5.2 mL) was irradiated for 70 min at 0 °C and resulted crude material was purified by column chromatography (silica gel, hexane/EtOAc = 6/1) to afford (*R*)-**10** (11.2 mg, 65%, 82% *ee*) as a while solid, **11** (1.6 mg, 9%) as a pale yellow solid, and (*S*)-**9** (0.9 mg, 5%) as a orange solid.



	tR/min	peak area	peak area%
(*R*)-**10**	8.642	6694151	90.844
(*S*)-**10**	9.842	674676	9.156

entry 10 (MeOH, –40 °C, 87% *ee*)

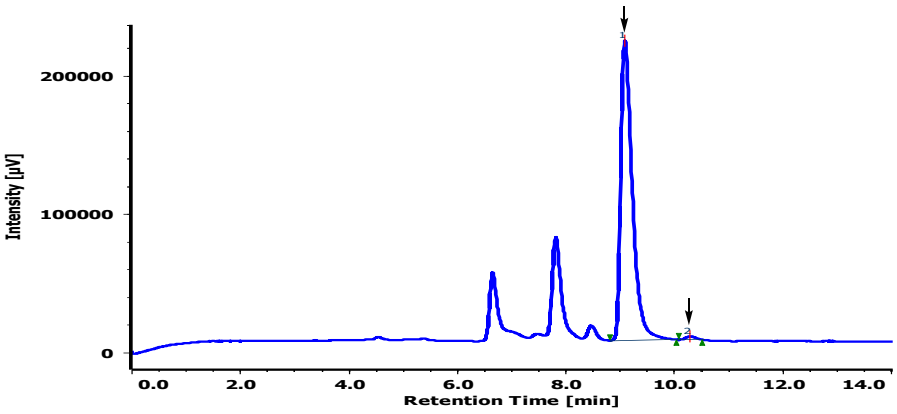
According to the synthesis of (*R*)-**10**, 1,2-quinone (*S*)-**9** (15.6 mg, 0.0467 mmol) in MeOH (4.7 mL) was irradiated for 2 h at –40 °C and resulted crude material was purified by column chromatography (silica gel, hexane/EtOAc = 6/1) to afford (*R*)-**10** (10.9 mg, 70%, 87% *ee*) as a while solid, **11** (1.6 mg, 10%) as a pale yellow solid, and (*S*)-**9** (1.2 mg, 8%) as a orange solid.



	tR/min	peak area	peak area%
(*R*)-**10**	8.575	7604086	93.608
(*S*)-**10**	9.742	519264	6.392

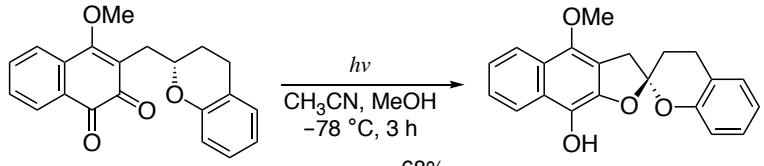
entry 11 (MeOH, –78 °C, 98% *ee*)

According to the synthesis of (*R*)-**10**, 1,2-quinone (*S*)-**9** (12.4 mg, 0.0371 mmol) in MeOH (3.7 mL) was irradiated for 3 h at –78 °C and resulted crude material was purified by column chromatography (silica gel, hexane/EtOAc = 6/1) to afford (*R*)-**10** (4.2 mg, 34%, 98% *ee*) as a while solid and (*S*)-**9** (3.6 mg, 29%) as a orange solid.



	tR/min	peak area	peak area%
(*R*)-**10**	9.075	3198076	99.141
(*S*)-**10**	10.267	27696	0.859

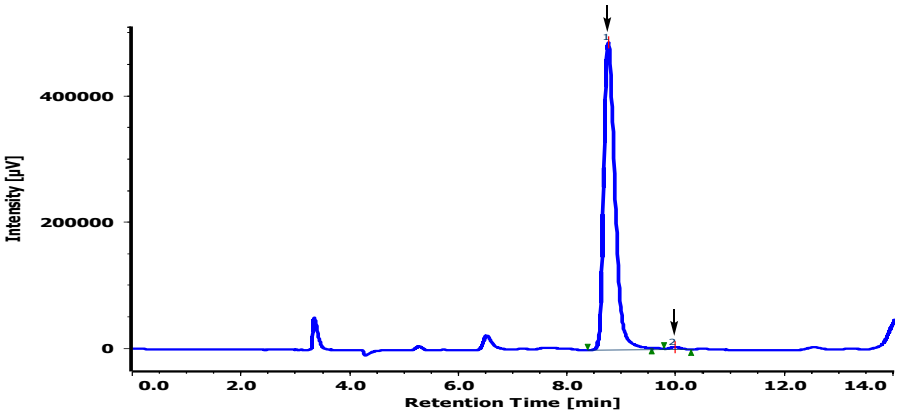
entry 12 (MeOH/CH_3CN = 3/1, –78 °C, 98% *ee*)



(*S*)-**9** (>99% *ee*) (*R*)-**10**

According to the synthesis of (*R*)-**10**, 1,2-quinone (*S*)-**9** (12.6 mg, 0.0377 mmol) in CH_3CN (0.94 mL) and MeOH (2.8 mL) was irradiated for 3 h at –78 °C and resulted crude material was purified by column chromatography (silica gel, hexane/EtOAc = 6/1) to afford (*R*)-**10** (8.6 mg, 68%, 98% *ee*) as a while solid and (*S*)-**9** (1.7 mg, 13%) as an orange solid.

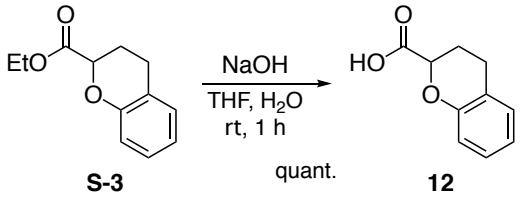
spiroacetal (*R*)-**10** (98% *ee*): mp 153 °C (decomp.); $[\alpha]_D^{20}$ –159 (*c* 0.210, $CHCl_3$).



	tR/min	peak area	peak area%
(*R*)-**10**	8.742	7002934	99.163
(*S*)-**10**	9.975	59120	0.837

For the determination of absolute stereochemistry

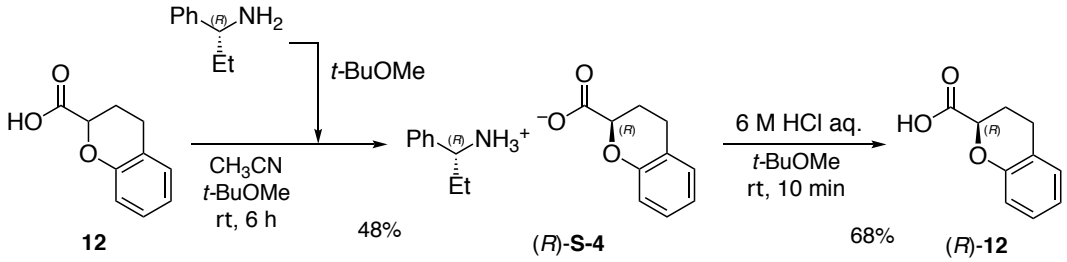
carboxylic acid **12**



To a solution of **S-3** (1.35 g, 6.55 mmol) in H_2O (24 mL) and THF (6.0 mL) was added NaOH (10.5 g, 26.3 mmol) at room temperature. After stiring for 1 h, the reaction was washed with Et_2O (×3). The aqueous layer was acidified by adding aqueous 1 M HCl at 0 °C. The mixture was extracted with *t*-BuOMe (×3), and the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. This crude material was used for the next experiment without further purification. Spectroscopic data were identical with reported data.[2]

carboxylic acid **12**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.13–2.21 (m, 1H), 2.35–2.43 (m, 1H), 2.77–2.86 (m, 1H), 2.86–2.94 (m, 1H), 4.74 (dd, 1H, *J* = 8.6, 3.4 Hz), 6.92 (t, 1H, *J* = 7.4 Hz), 6.93 (d, 1H, *J* = 8.2 Hz), 7.07 (d, 1H, *J* = 7.4 Hz), 7.17 (t, 1H, *J* = 8.2 Hz), 10.6 (brs, 1H).

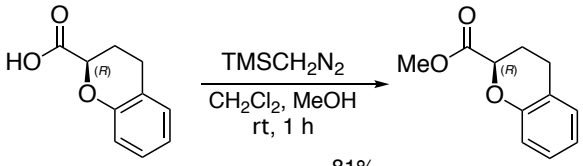
carboxylic acid (*R*)-**12**



To a solution of **12** (97.4 mg, 0.547 mmol) in CH_3CN (490 μL) and *t*-BuOMe (420 μL) was added (*R)*-(–)-1-phenylpropylamine (50 μL, 0.0348 mmol) in *t*-BuOMe (80 μL) dropwise at room temperature. The reaction mixture was seeded with white precipitate. After stiring for 0.5 h, the reaction was diluted with *t*-BuOMe (400 μL) and the mixture was further stirred for 5.5 h. The mixture was filtered and the filter cake was rinsed with *t*-BuOMe to afford (*R*)-**S-4** (80.3 mg, 48%) as a white solid. This crude material was used for the next experiment without further purification. To a solution of the crude material, including (*R*)-**S-4** (80.3 mg, 0.263 mmol), in *t*-BuOMe (1.1 mL) was added aqueous 6 M HCl (0.930 mL) at room temperature. After stiring for 10 min, the mixture was extracted with *t*-BuOMe (×3), and the combined organic extracts were dried ($MgSO_4$), and concentrated in vacuo to afford the caboxylic acid (*R*)-**12** (32.5 mg, 68%, 33% from caboxylic acid **12**). Spectroscopic data were identical with reported data.[3]

caboxylic acid (*R*)-**12**: $[\alpha]_D^{20}$ –4.1 (*c* 0.67, MeOH), lit. $[\alpha]_D^{20}$ –6.3 (*c* 1.05, MeOH).

methyl ester (*R*)-**S-5**

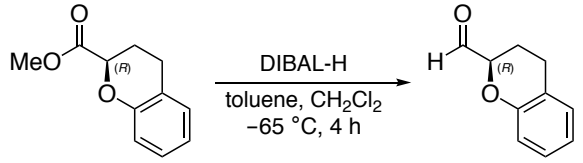


(*R*)-**12** (*R*)-**S-5**

To a solution of (*R*)-**12** (30.1 mg, 0.169 mmol) in CH_2Cl_2 (400 μL) and MeOH (40 μL) was added trimethylsilyldiazomethane (0.60 M solution in hexane, 340 μL, 0.203 mmol) at room temperature. The reaction was concentrated in vacuo. The residue was purified by PTLC (silica gel, hexane/EtOAc = 3/1) to afford methyl ester (*R*)-**S-5** (25.8 mg, 81%) as a colorless oil. Spectroscopic data were identical with reported data.[4]

methyl ester (*R*)-**S-5**: R_f 0.49 (hexane/EtOAc = 4/1); $[\alpha]_D^{20}$: –4.9 (*c* = 2.0, $CHCl_3$), lit. $[\alpha]_D^{20}$ –6.9, (*c* 3.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.15–2.23 (m, 1H), 2.25–2.32 (m, 1H), 2.72–2.80 (m, 1H), 2.81–2.89 (m, 1H), 3.80 (s, 3H), 4.74 (dd, 1H, *J* = 7.7, 3.5 Hz), 6.87 (td, 1H, *J* = 7.4, 1.1 Hz), 6.93 (dd, 1H, *J* = 8.2, 0.8 Hz), 7.03 (d, 1H, *J* = 7.4 Hz), 7.12 (t, 1H, *J* = 8.2 Hz).

aldehyde (*R*)-**4**

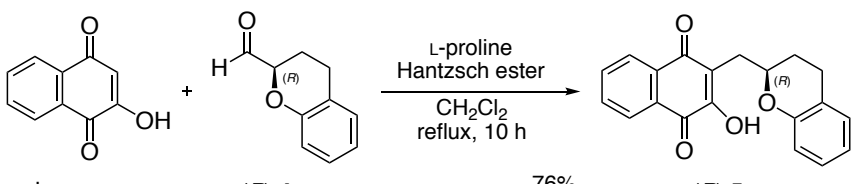


(*R*)-**S-5** (*R*)-**4**

To a solution of (*R*)-**S-5** (25.8 mg, 0.125 mmol) in toluene (200 μL) and CH_2Cl_2 (50 μL) was added DIBAL-H (0.61 M solution in hexane, 220 μL, 0.131 mmol) at –65 °C. After stiring for 4 h at –65 °C, the reaction was stopped by adding MeOH (100 μL) at –65 °C and allowed to warm to room temperature. The mixture was filtered through a Celite® pad (rinsed with CH_2Cl_2) and washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 2/1) to afford aldehyde (*R*)-**4** (18.8 mg, 93%) as a pale yellow oil. Spectroscopic data were identical with reported data.[2]

aldehyde (*R*)-**4**: $[\alpha]_D^{20}$: –79 (*c* = 0.56, $CHCl_3$).

hydroxynaphthoquinone (*R*)-**5**



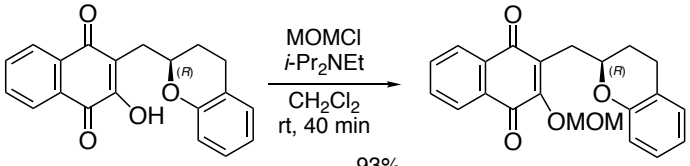
lawsone (*R*)-**4** (*R*)-**5**

To a solution of (*R*)-**4** (18.8 mg, 0.116 mmol) in CH_2Cl_2 (2 mL) was added lawsone (36.3 mg, 0.209 mmol),

L-proline (6.7 mg, 0.058 mmol) and Hantzsch ester (29.4 mg, 0.116 mmol) at room temperature. After refluxed for 10 h, the mixture was concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 6/1) to afford hydroxynaphthoquinone (*R*)-**5** (29.1 mg, 78%) as an orange solid.

hydroxynaphthoquinone (*R*)-**5**: $[\alpha]_D^{20}$: –73 (*c* = 0.60, $CHCl_3$).

naphthoquinone (*R*)-**6**

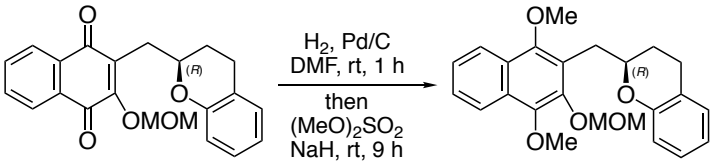


(*R*)-**5** (*R*)-**6**

To a solution of (*R*)-**5** (16.0 mg, 0.0500 mmol) in CH_2Cl_2 (250 μL) was added *i*-Pr_2NEt (18 μL, 0.10 mmol) and MOMCl (6.0 μL, 0.080 mmol) at room temperature. After stirring for 40 min, the reaction was quenched by adding saturated aqueous $NaHCO_3$ at 0 °C. The mixture was extracted with CH_2Cl_2 (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 5/1) to afford naphthoquinone (*R*)-**6** (16.6 mg, 91%) as a yellow oil.

naphthoquinone (*R*)-**6**: $[\alpha]_D^{20}$: –49 (*c* = 0.49, $CHCl_3$).

naphthalene (*R*)-**7**

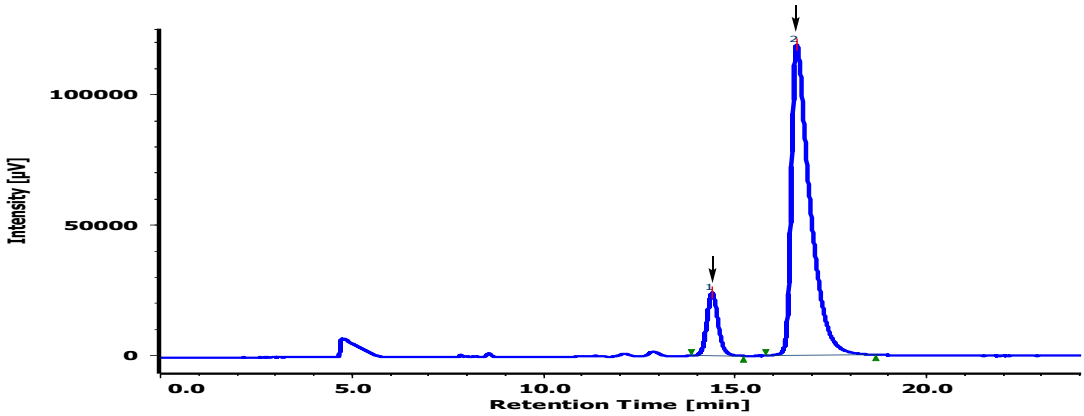


(*R*)-**6** (*R*)-**7**

A flask, thoroughly purged with argon, was charged with 10% Pd/C (1.5 mg), to which was added a solution of naphthoquinone (*R*)-**6** (14.7 mg, 0.0403 mmol) in DMF (200 μL) at room temperature. The atmosphere was changed from argon to H_2 (1 atm), and the mixture was vigorously stirred for 1 h at room temperature. After changing the atmosphere from H_2 to argon, the mixture was added NaH (63% dispersion in oil, 6.1 mg, 0.161 mmol) and $(MeO)_2SO_2$ (8.0 μL, 0.084 mmol). The atmosphere was changed from argon to H_2 (1 atm), and the mixture was vigorously stirred for 9 h at room temperature. After changing the atmosphere from H_2 to argon, the mixture was stopped by adding diethylamine (42 μL, 0.40 mmol) and water at 0 °C and filtered through a Celite® pad (rinsed with EtOAc). The mixture was extracted with EtOAc (×3), and the combined organic extracts were washed with saturated aqueous NH_4Cl, and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by PTLC (silica gel, hexane/EtOAc = 4/1) to afford naphthalene (*R*)-**7** (14.4 mg, 91%, 78% *ee*) as a pale

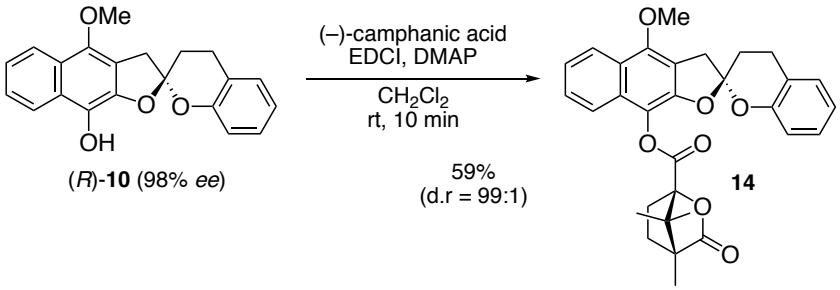
yellow oil.

Enantiomeric purity of (*R*)-**7** was also assessed by HPLC analysis on a chiral stationary phase [DAICEL CHIRALPAK® IF (0.46 cm φ × 25 cm), UV detection at 254 nm, hexane/*i*-PrOH= 99/1, flow rate 1.0 mL/min, t_R =14.4 min for (*S*)-isomer, and 16.6 min for (*R*)-isomer]



	tR/min	peak area	peak area%
(*S*)-**7**	14.383	492693	10.978
(*R*)-**7**	16.592	3995147	89.022

ester (*R*)-**14**



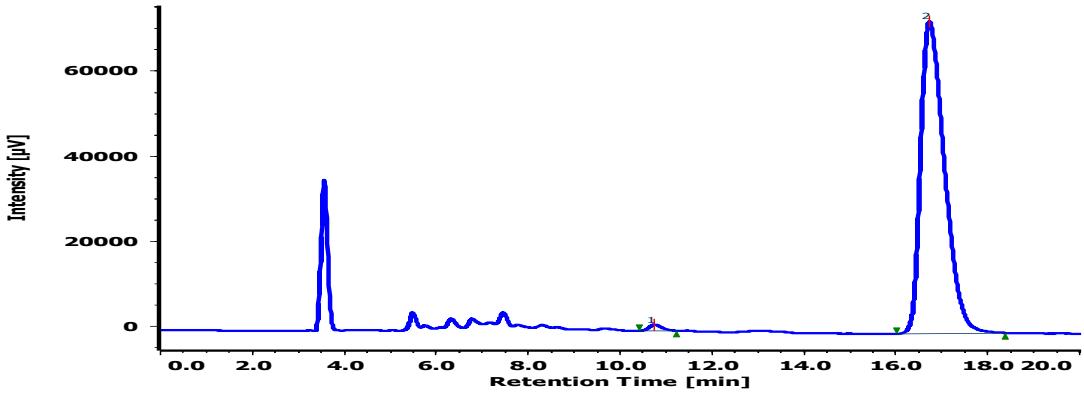
To a solution of spiroacetal (*R*)-**10** (7.5 mg, 0.022 mmol) in CH_3CN (0.70 mL) was added DMAP (1.4 mg, 0.0068 mmol), (–)-camphanic acid (13.0 mg, 0.0656 mmol) and EDCI (9.5 mg, 0.050 mmol) at room temperature. After stirring for 10 min, the reaction was quenched by adding saturated aqueous NH_4Cl and poured into mixed solvent of water and CH_2Cl_2. The mixture was extracted with CH_2Cl_2 (×3), and the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by PTLC (silica gel, hexane/acetone = 2/1) to afford ester **14** (6.8 mg, 59%, d.r. = 99:1) as a white solid. Recrystallization from hexane/EtOAc (3/1) afforded ester **14** as white needles.

ester **14**: R_f 0.43 (hexane/EtOAc = 3/1); mp 188–189 °C (hexane/EtOAc); $[\alpha]_D^{20}$: –18 (*c* = 0.22, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.67 (s, 3H), 1.05 (s, 3H), 1.09 (s, 3H), 1.71 (ddd, 1H, *J* = 13.2, 9.0, 4.2 Hz), 1.93 (ddd, 1H, *J* = 13.2, 10.8, 4.8 Hz), 2.15 (ddd, 1H, *J* = 13.2, 9.0, 4.2 Hz), 2.29 (ddd, 1H, *J* = 13.2, 13.2, 6.0 Hz), 2.43 (ddd, 1H,

J = 12.0, 6.6, 2.7 Hz), 2.53 (ddd, 1H, *J* = 13.2, 10.8, 4.2 Hz), 2.87 (dd, 1H, *J* = 16.8, 6.0 Hz), 3.18 (ddd, 1H, *J* = 16.8, 13.2, 6.0 Hz), 3.61 (d, 1H, *J* = 16.8 Hz), 3.81 (d, 1H, *J* = 16.8 Hz), 4.10 (s, 3H), 6.77 (d, 1H, *J* = 7.8 Hz), 6.91 (dd, 1H, *J* = 7.8, 7.2 Hz), 7.08 (d, 1H, *J* = 7.2 Hz), 7.09 (dd, 1H, *J* = 7.8, 7.2 Hz), 7.31 (dd, 1H, *J* = 7.8, 7.2 Hz), 7.46 (dd, 1H, *J* = 7.8, 7.2 Hz), 7.69 (d, 1H, *J* = 8.4 Hz), 8.12 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 9.8, 16.0, 16.6, 21.9, 29.0, 30.2, 30.5, 40.8, 54.5, 54.8, 60.0, 91.3, 110.3, 114.2, 117.4, 119.8, 120.9, 121.6, 121.8, 122.3, 123.8, 124.1, 127.0, 127.6, 128.4, 128.9, 146.9, 150.1, 152.0, 164.8, 178.1; IR (neat) 2970, 2931, 1778, 1656, 1585, 1490, 1435, 1364, 1304, 1255, 1223, 1176, 1092, 1058, 1042, 982, 949, 914, 828, 755 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{31}O_7$ ($[M+H]^+$) *m/z* 515.2064, found *m/z* 515.2081.

Diastereomeric purity of (*R*)-**14** was assessed by HPLC analysis on a chiral stationary phase [DAICEL CHIRALPAK® IF (0.46 cm φ × 25 cm), UV detection at 254 nm, hexane/*i*-PrOH = 55/45, flow rate 1.0 mL/min, t_R =10.7 min for (*S*)-isomer, and 16.7 min for (*R*)-isomer]

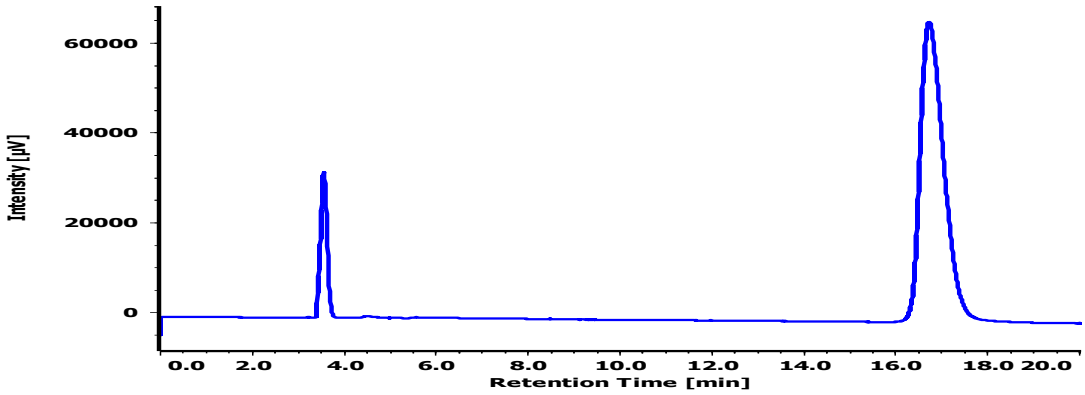
HPLC analysis of **14** before recrystallization



	tR/min	peak area	peak area%
*diastereomer	10.742	28857	1.080
14	16.708	2643541	98.920

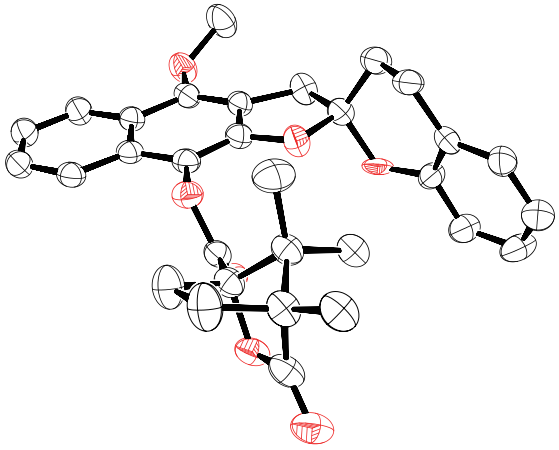
*The retention time for the diastereomer of **14** was confirmed by comparison with the chromatogram obtained from esterification of (*R*)-**10**, which has low enantiomeric purity.

HPLC analysis of the crystal employed for X-ray diffraction analysis



Crystallographic data: $C_{31}H_{30}O_7$ (ester **14**) + 0.285 C_6H_{14} (hexane), Formula Weight = 539.11, 0.187×0.059×0.049 mm, hexagonal, space group *P* 6_1, Z = 6, Z' = 1, T = 93 K, *a* = 19.2800(3), *b* = 19.2800(3), *c* = 12.8484(2) Å, V = 4136.12(14) $Å^3$, λ(CuKα) = 1.54186, μ = 0.739 mm^{-1}, Intensity data were collected on RIGAKU R-AXIS RAPID-II IP area detector system. The structure was solved by direct methods and refined by the full-matrix least-squares on F^2 (SHELXL-2016'). A total of 48965 reflections were measured and 4914 were independent. Final *R*1 = 0.0370, *wR*2 = 0.0955 (4338 refs, $I > 2s$ (*I*)), and GOF = 1.035 (for all data, *R*1 = 0.0441, *wR*2 = 0.1004). Flack Parameter = –0.02(5).

X-ray structure of **14** (solvent and disordered atoms are omitted for clarity)



References

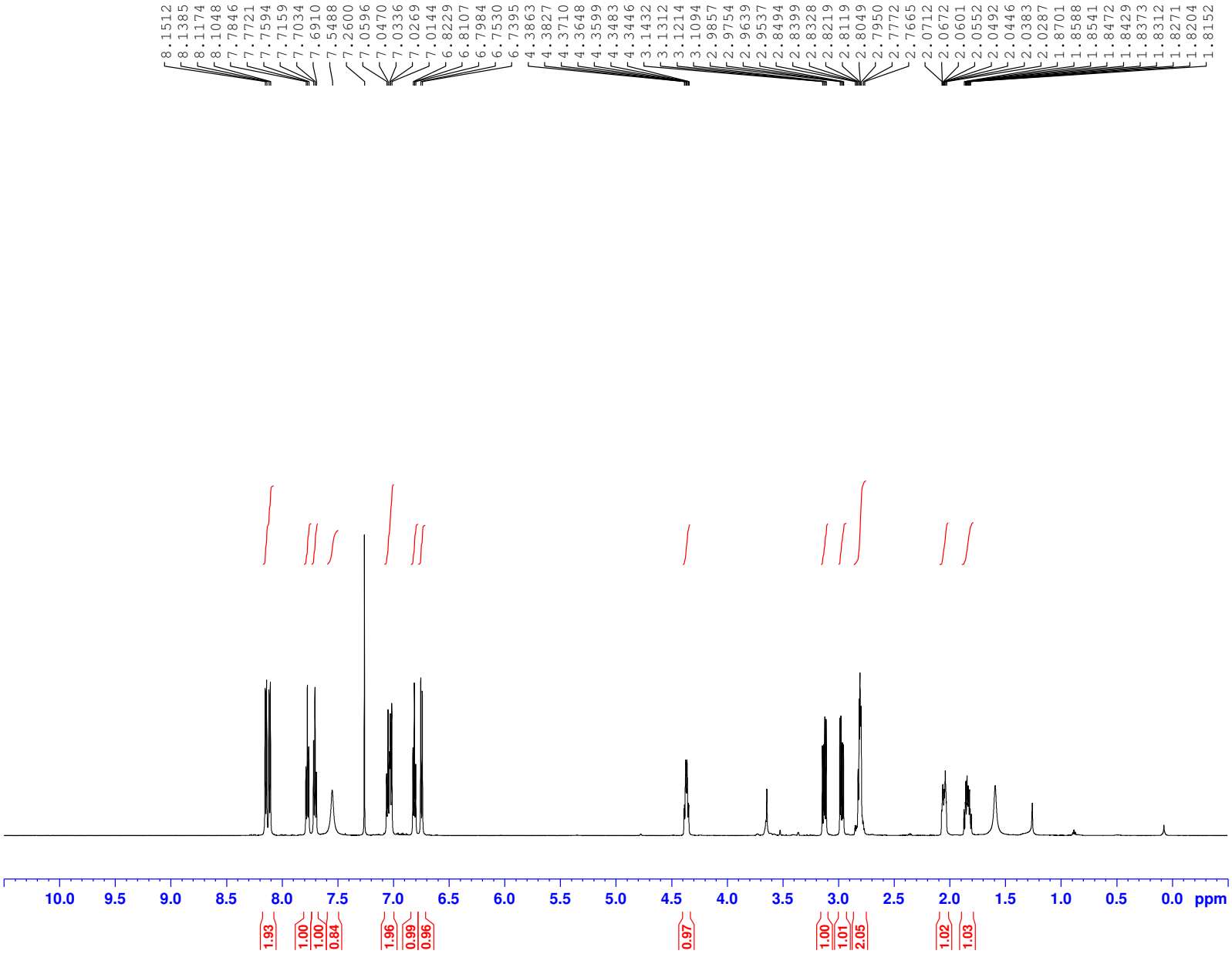
[1] Velema, W. A.; van der Toorn, M.; Szymanski, W.; Feringa, B. L. *J. Med. Chem.* **2013**, *56*, 4456–4464.

[2] Kwak, J.-H.; Won, S.-W.; Kim, T.-J.; Roh, E.; Kang, H.-Y.; Lee, H.-W.; Jung, J.-K.; Hwang, B.-Y.; Kim, Y.; Cho, J.; Lee, H. *Arch. Pharm. Res.* **2008**, *31*, 133–141.

[3] a) Gontcharov, A. V.; Nikitenko, A. A.; Raveendranath, P.; Shaw, C.-C.; Wilk, B. K.; Zhou, D. WO Patent 123941 A2, **2007**. b) Shukla, M. R.; Sarde, A. G.; Loriya, R. M.; Pachpute, V. D.; Walke, N. B.; Khan, T. H.; Kulkarni, S. A.; Palle, V. P.; Kamboj, R. K. WO Patent 124828 A1, **2013**.

[4] Kim, D. W.; Alam, M. M.; Lee, Y. H.; Khan, M. N. A.; Zhang, Y.; Lee, Y. S. *Tetrahedron: Asymmetry* **2015**, *26*, 912–917.

^{1}H NMR (600 MHz, $CDCl_3$)

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FIDRES             0.183399 Hz
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RG                     31.94
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TE                    300.0 K
D1              1.00000000 sec
TD0                        1

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PLW1           23.00000000 W

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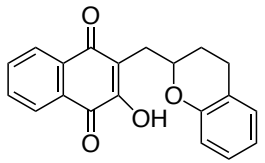
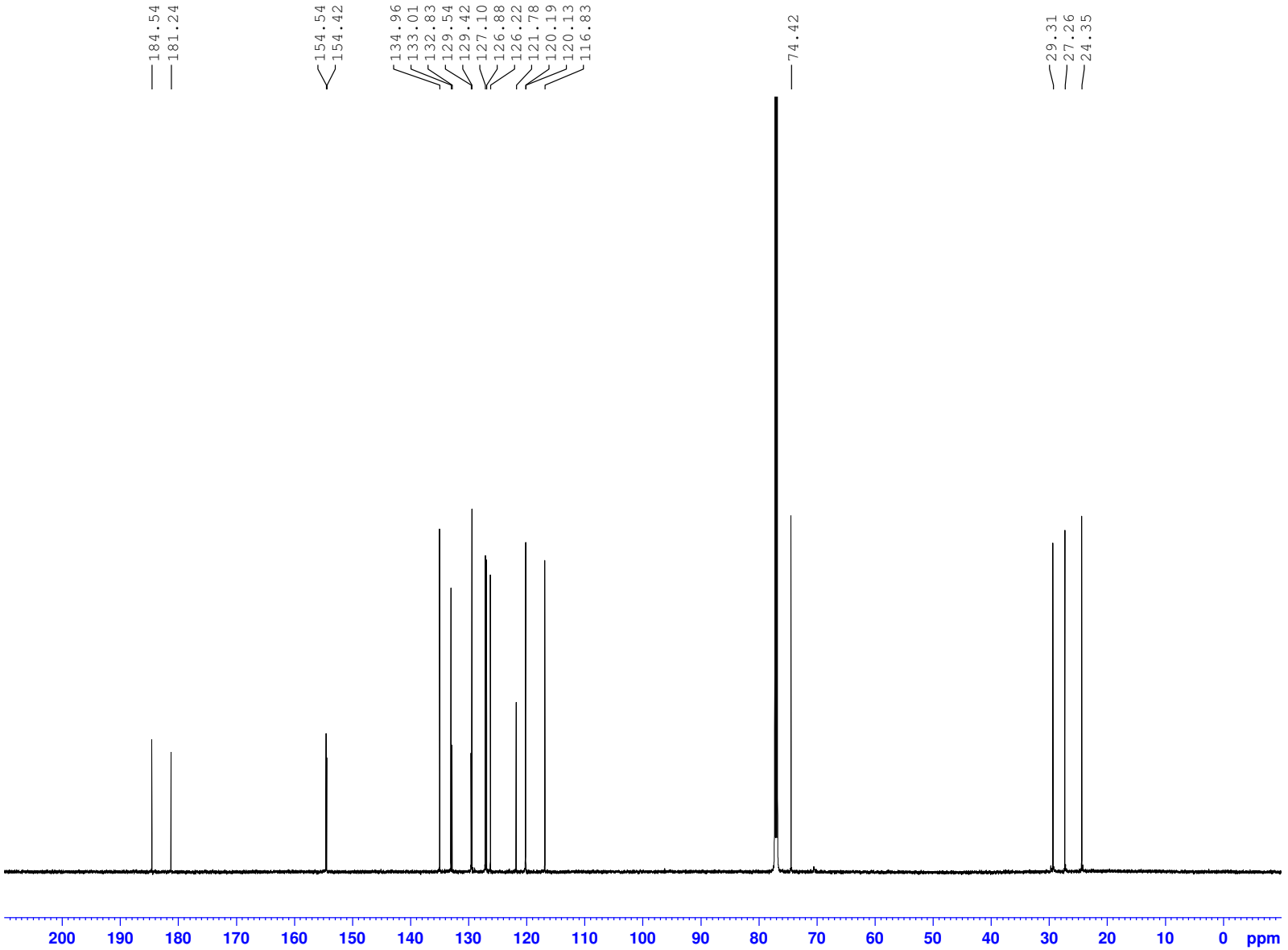


5

^{13}C NMR (150 MHz, $CDCl_3$)

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PCPD2                  70.00 usec
PLW2             26.00000000 W
PLW12             0.76407999 W
PLW13             0.37439999 W

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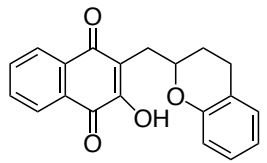
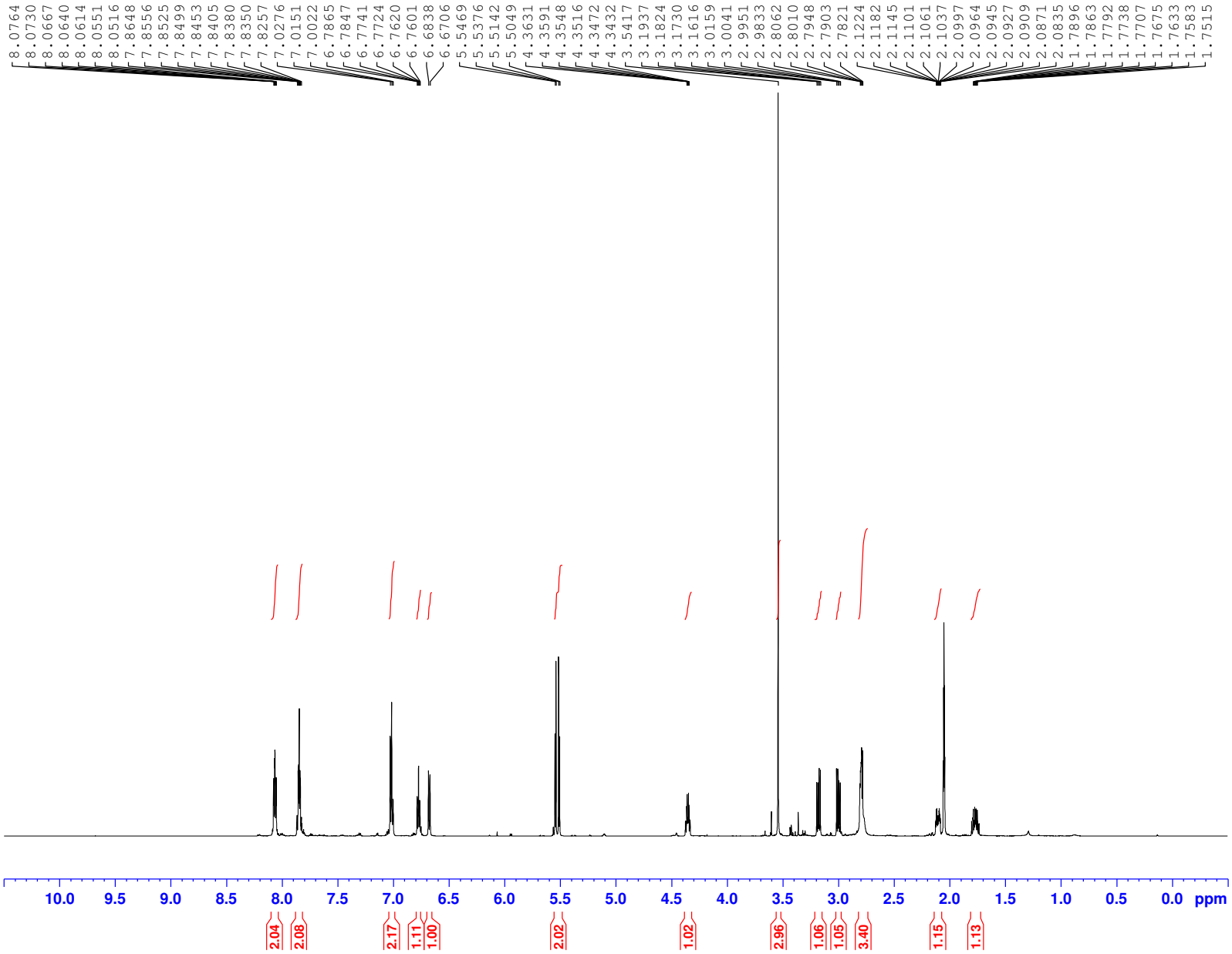


5

^{1}H NMR (600 MHz, acetone-d_6)

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NUC1                       1H
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PLW1             23.00000000 W

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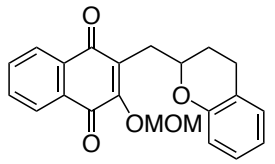
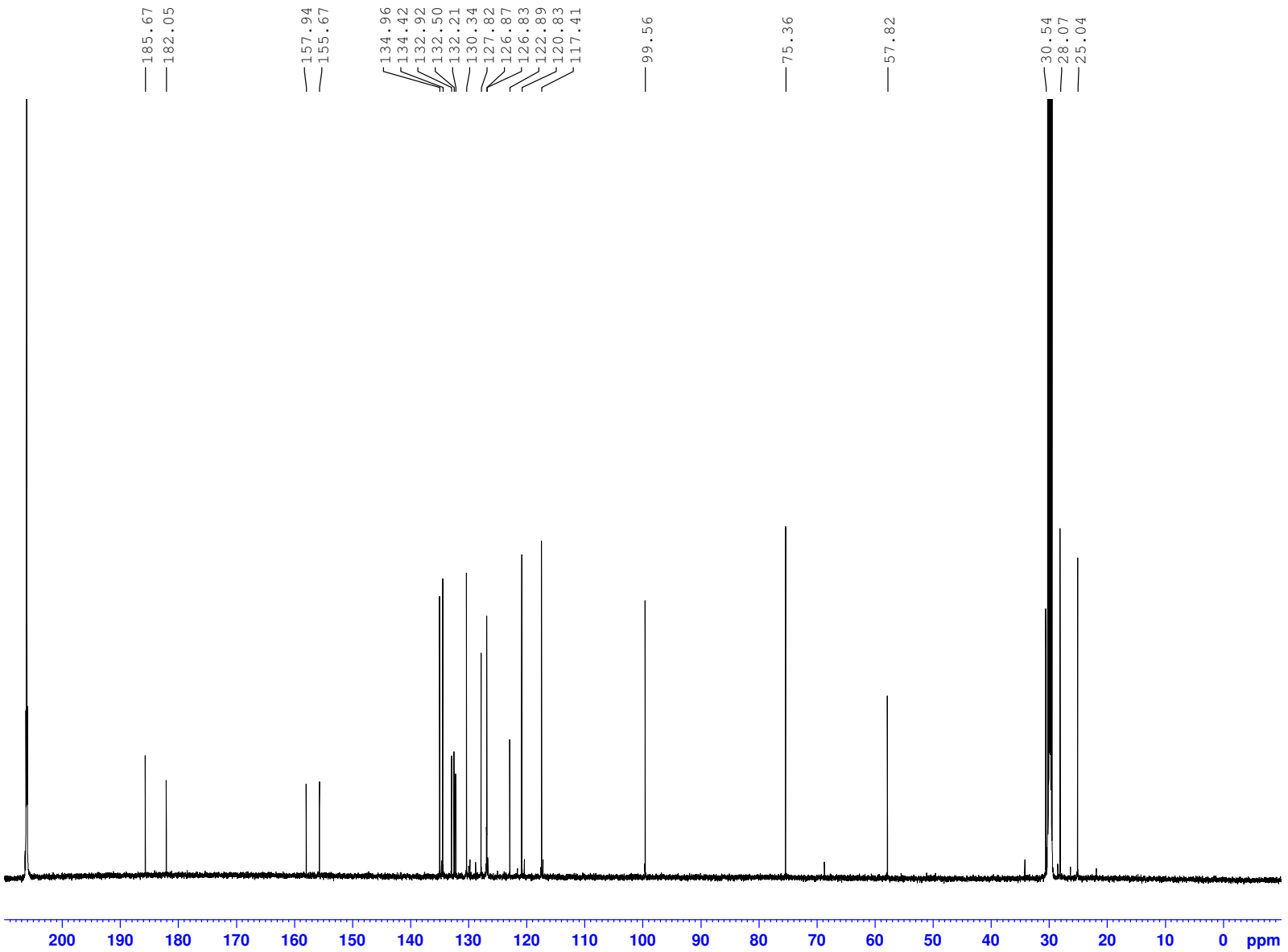


6

^{13}C NMR (150 MHz, acetone-d_6)

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D11               0.03000000 sec
TD0                           1

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PLW1             70.00000000 W

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PLW12             0.76407999 W
PLW13             0.37439999 W

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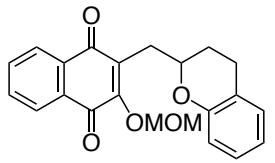
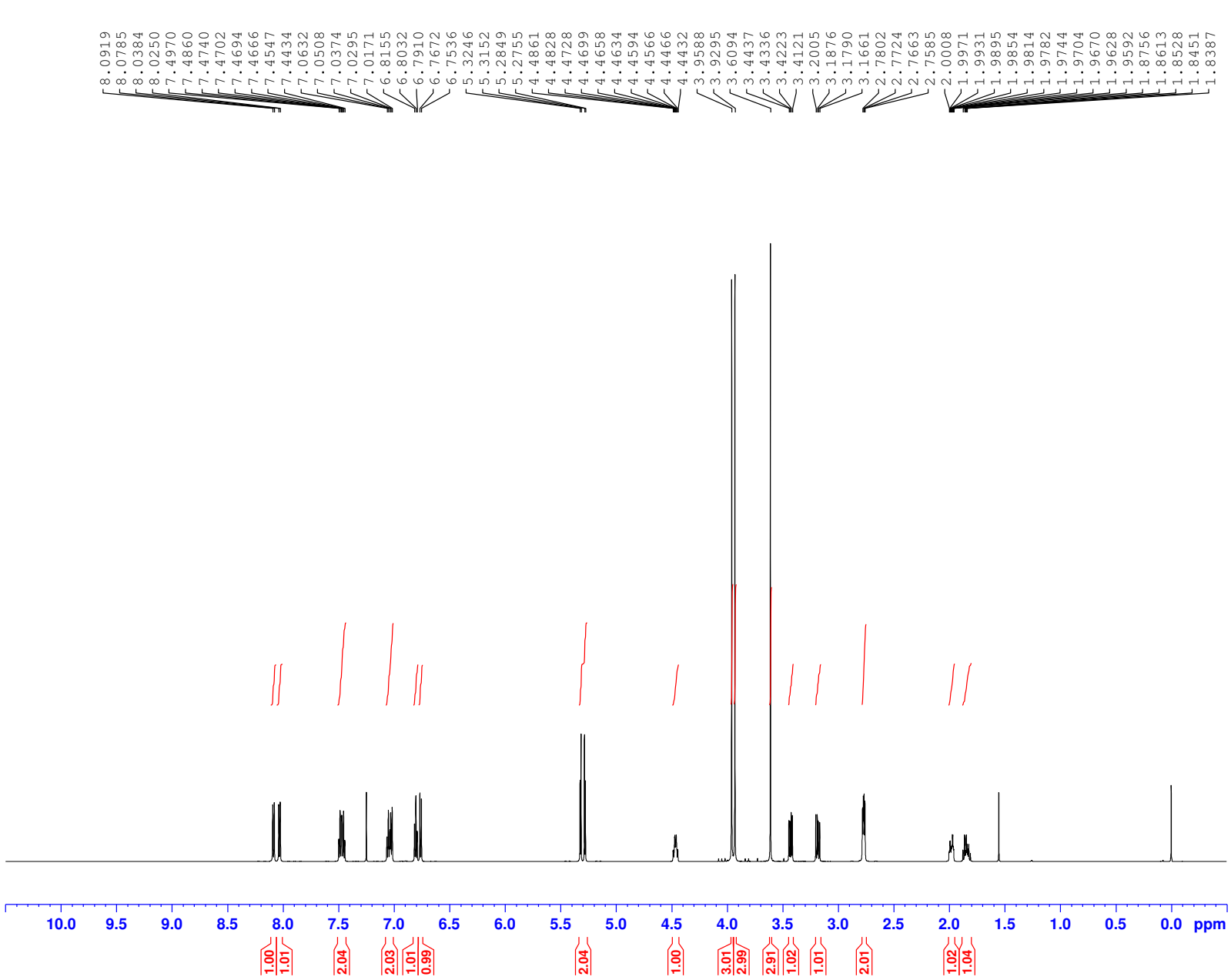


6

^{1}H NMR (600 MHz, $CDCl_3$)



BRUKER

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TE                       300.0 K
D1                  1.00000000 sec
TD0                         1

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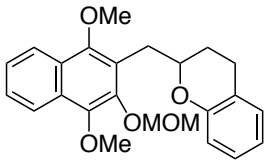
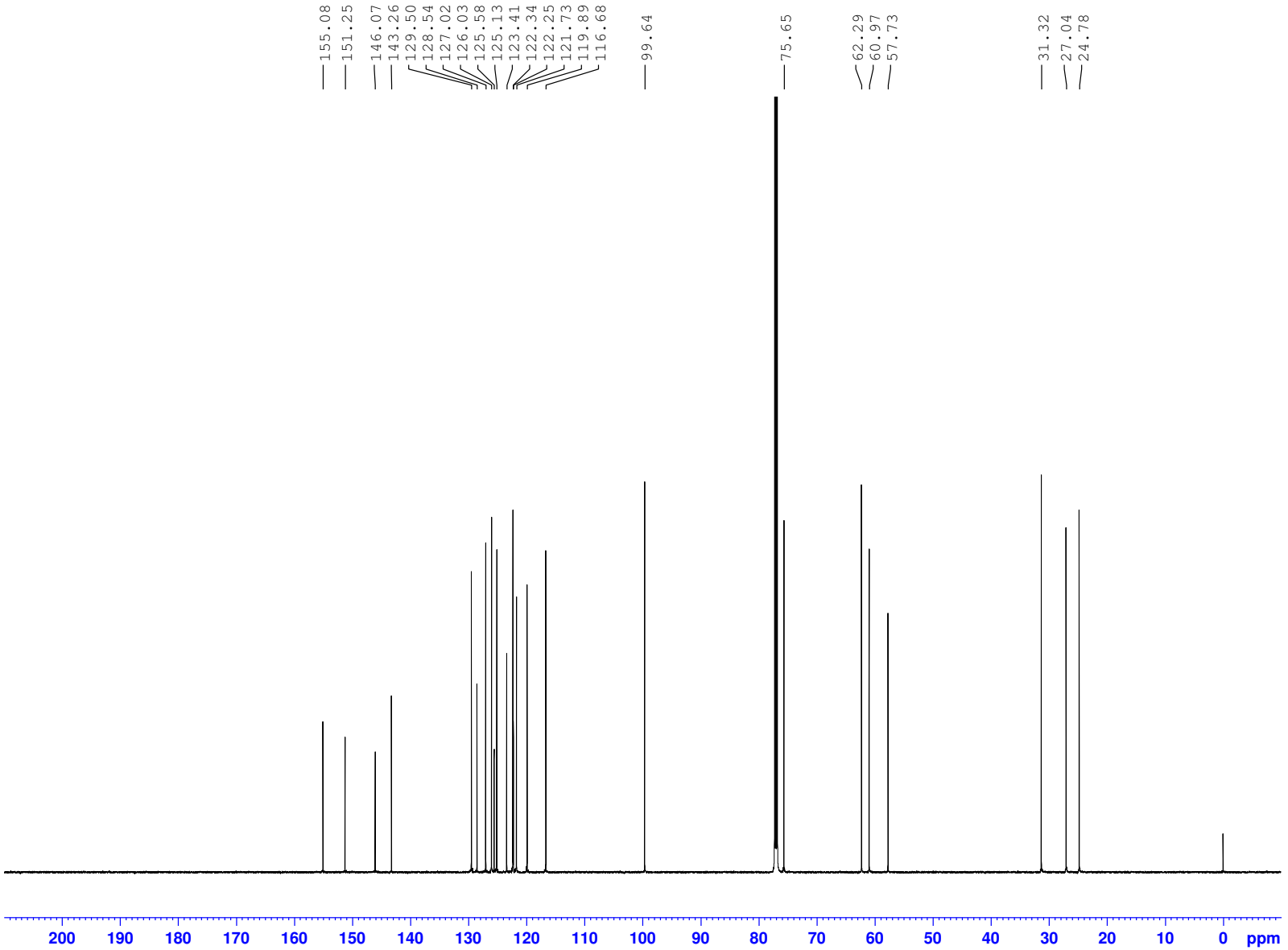
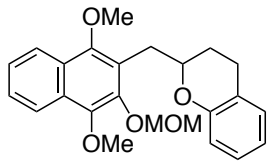


7

^{13}C NMR (150 MHz, $CDCl_3$)

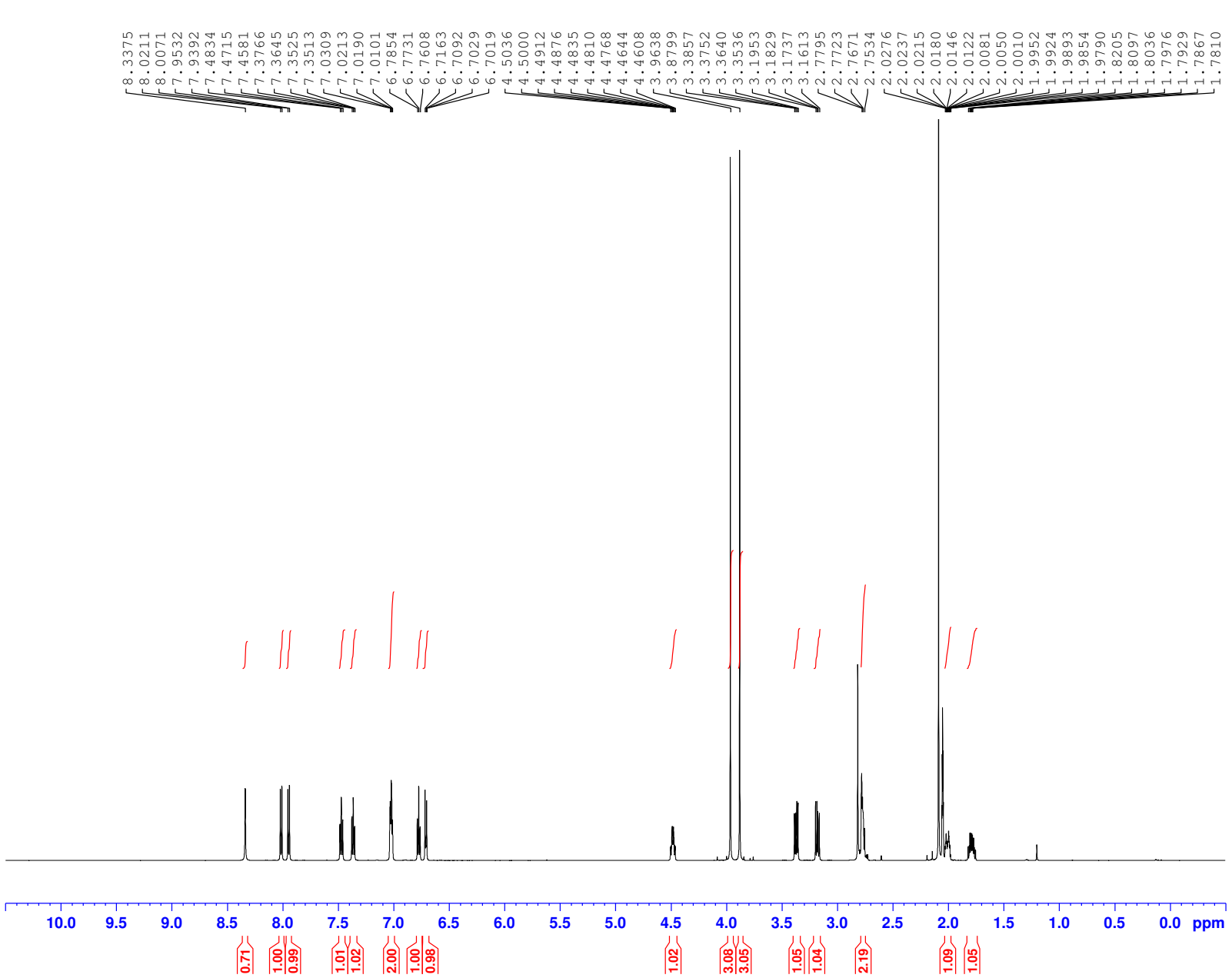



```
Current Data Parameters
NAME                  fw1-1326
EXPNO                       31
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20180108
Time                     19.19
INSTRUM                  spect
PROBHD    5 mm CPPBBO BB
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        4096
DS                           4
SWH                  36057.691 Hz
FIDRES                0.550197 Hz
AQ                    0.9087659 sec
RG                       175.56
DW                       13.867 usec
DE                       18.00 usec
TE                       300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               150.9178981 MHz
NUC1                       13C
P1                       10.00 usec
PLW1               70.00000000 W

======== CHANNEL f2 ========
SFO2               600.1324005 MHz
NUC2                       1H
CPDPRG[2                waltz16
PCPD2                    70.00 usec
PLW2               14.00000000 W
PLW12               0.64286000 W
PLW13               0.32335001 W

F2 - Processing parameters
SI                        32768
SF                 150.9028106 MHz
WDW                          EM
SSB          0
LB                        1.00 Hz
GB           0
PC                        1.40
```

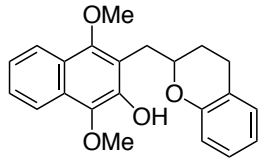


7

^{1}H NMR (600 MHz, acetone-d_6)

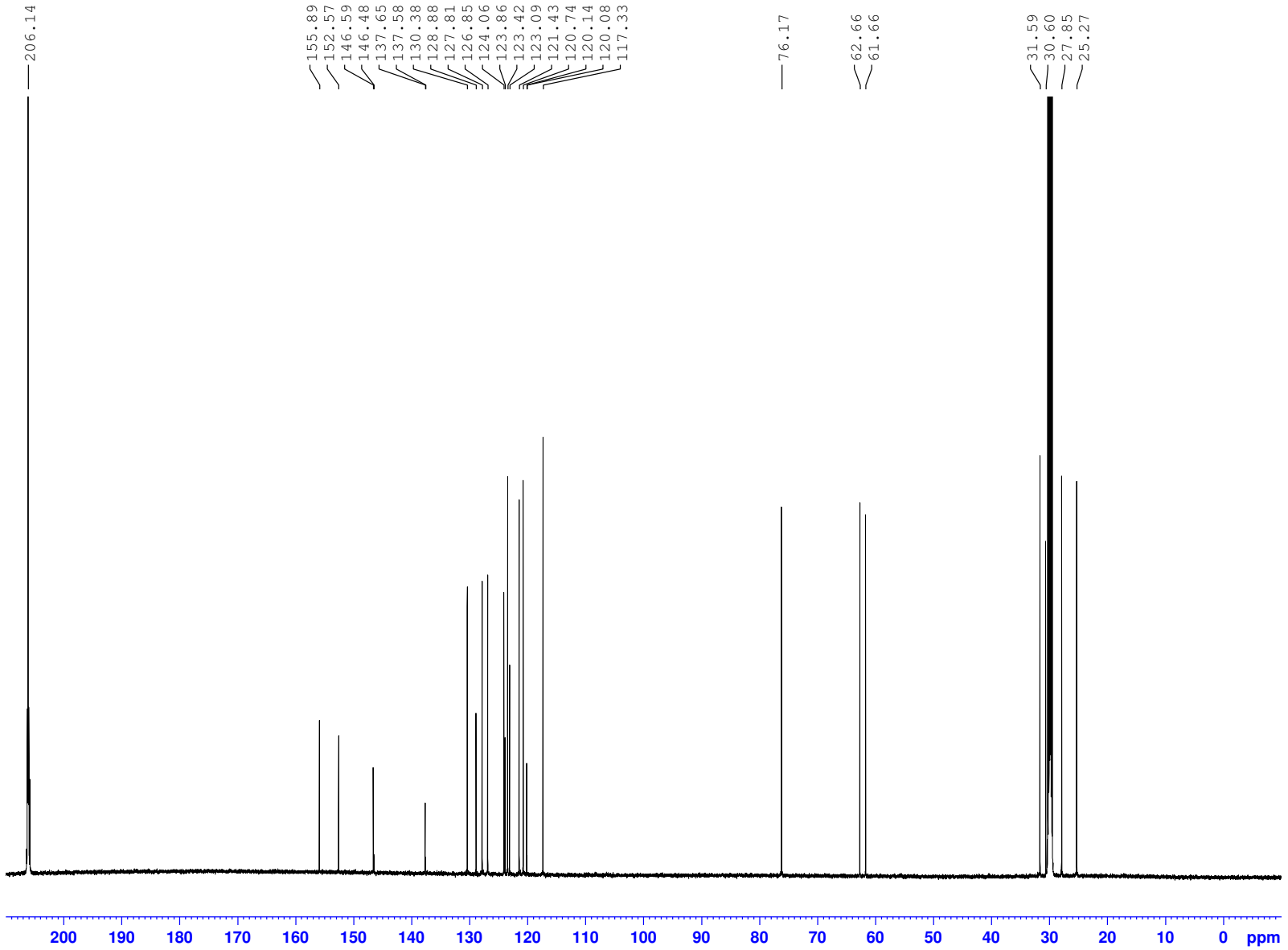


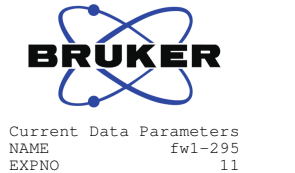

```
Current Data Parameters
NAME                  fw1-295
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20151211
Time                    3.16
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG                 zg30
TD                     65536
SOLVENT              Acetone
NS                        16
DS                         2
SWH                12019.230 Hz
FIDRES              0.183399 Hz
AQ                  2.7262976 sec
RG                      31.94
DW                     41.600 use
DE                     10.00 use
TE                     300.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             600.1337060 MHz
NUC1                      1H
P1                     12.00 use
PLW1             23.00000000 W

F2 - Processing parameters
SI                     65536
SF               600.1300126 MHz
WDW                       EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```



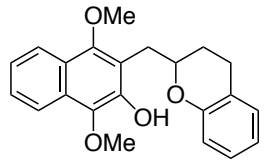
8

^{13}C NMR (150 MHz, acetone-d_6)



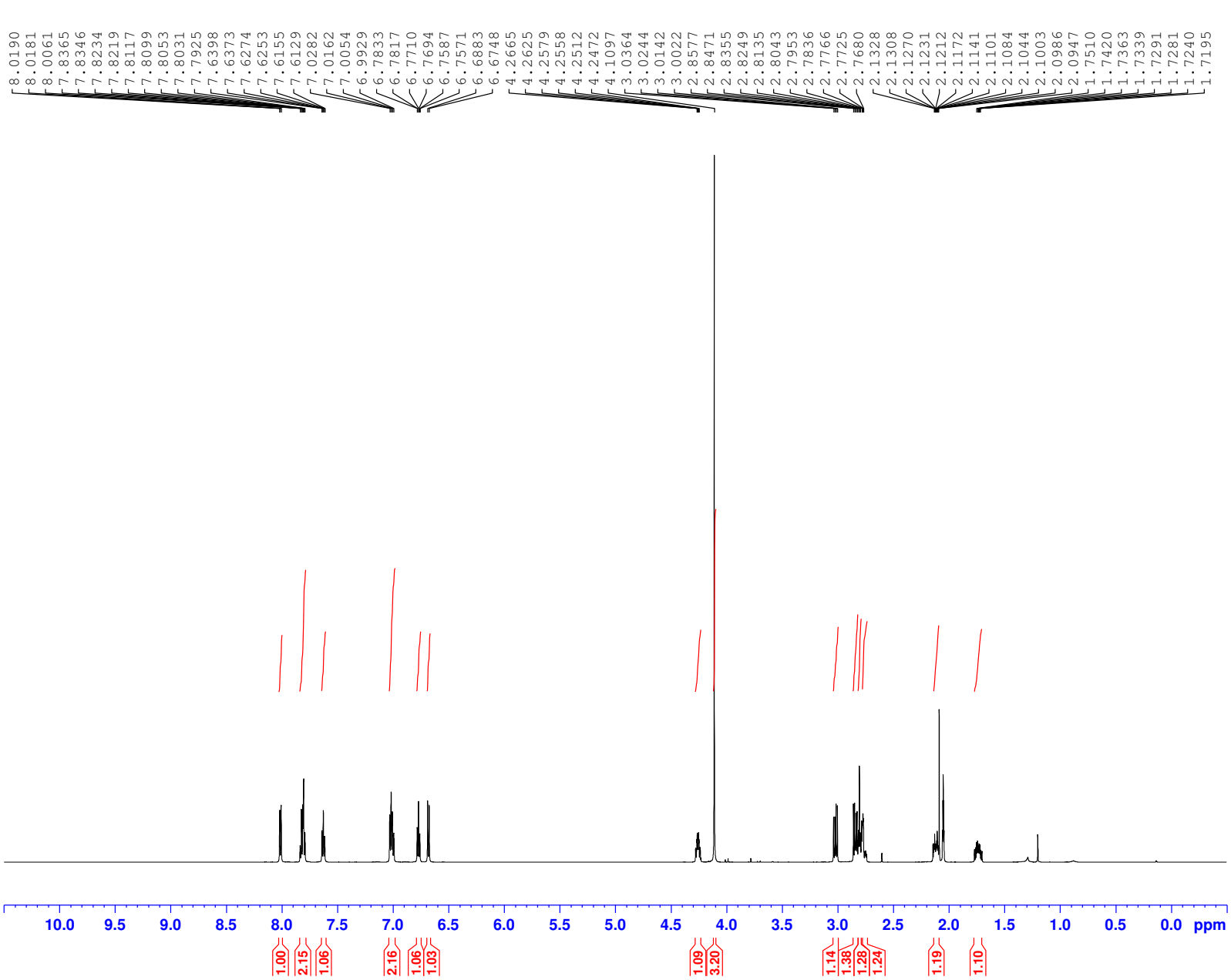



```
Current Data Parameters
NAME                  fw1-295
EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_               20151211
Time                    4.59
INSTRUM                spect
PROBHD   5 mm CPPBBO BB
PULPROG                zgpg30
TD                      65536
SOLVENT               Acetone
NS                         2048
DS                            4
SWH                 36057.691 Hz
FIDRES               0.550197 Hz
AQ                   0.9087659 sec
RG                      175.56
DW                      13.867 usec
DE                      18.00 usec
TE                      300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1               150.9178981 MHz
NUC1                       13C
P1                      10.00 usec
PLW1               70.00000000 W

======== CHANNEL f2 ========
SFO2               600.1324005 MHz
NUC2                       1H
CPDPRG[2                waltz16
PCPD2                   70.00 usec
PLW2               26.00000000 W
PLW12               0.76407999 W
PLW13               0.37439999 W

F2 - Processing parameters
SI                         32768
SF                 150.9026709 MHz
WDW                           EM
SSB              0
LB                      1.00 Hz
GB               0
PC                      1.40
```

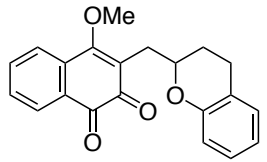


8

^{1}H NMR (600 MHz, acetone-d_6)

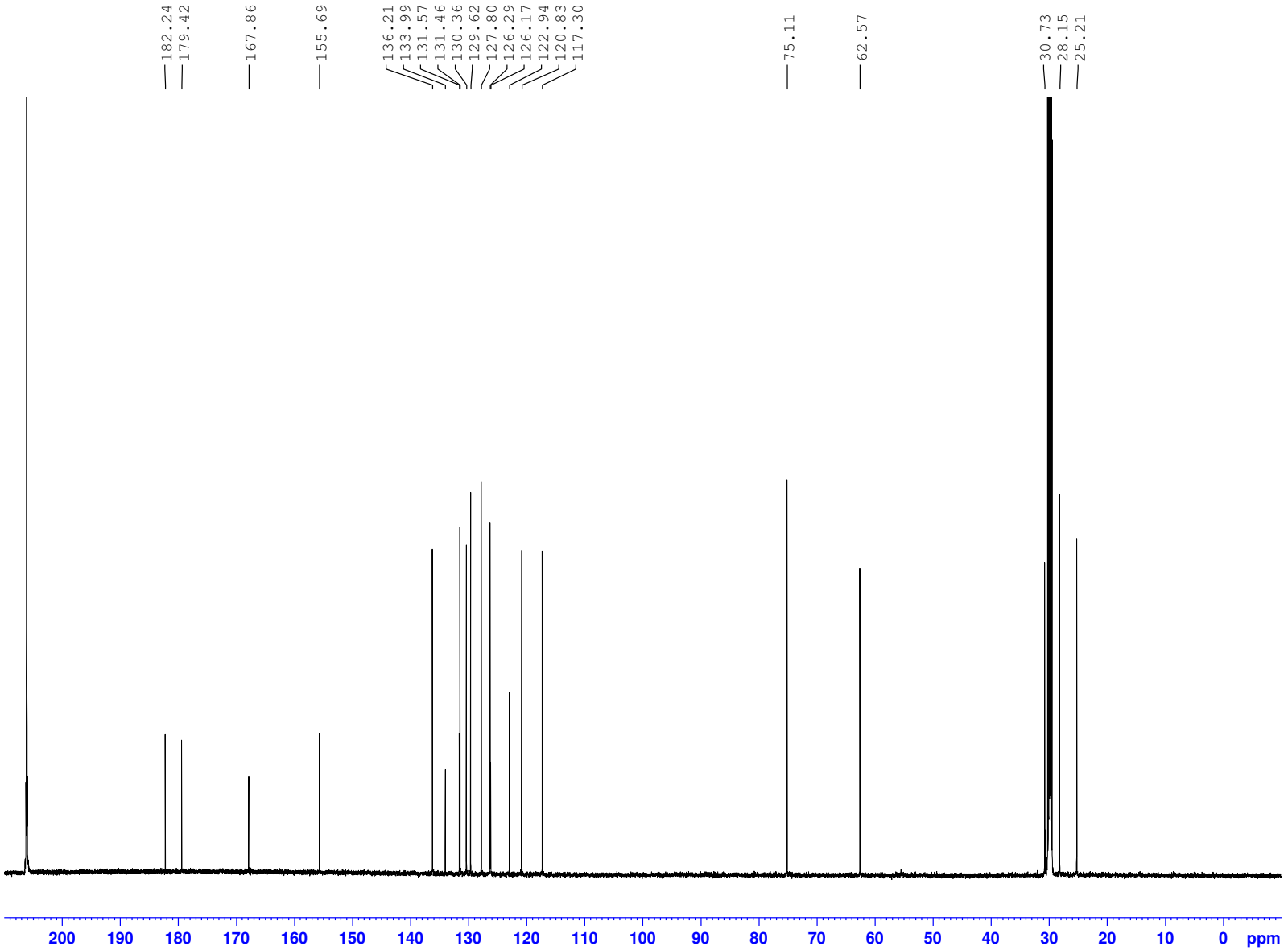


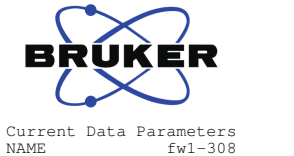

```
Current Data Parameters
NAME                  fw1-308
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20151219
Time                   19.39
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG                 zg30
TD                     65536
SOLVENT              Acetone
NS                        16
DS                         2
SWH                12019.230 Hz
FIDRES              0.183399 Hz
AQ                  2.7262976 sec
RG                     31.94
DW                     41.600 usec
DE                     10.00 usec
TE                     300.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1              600.1337060 MHz
NUC1                      1H
P1                     12.00 usec
PLW1              23.00000000 W

F2 - Processing parameters
SI                     65536
SF                600.1300124 MHz
WDW                       EM
SSB          0
LB                      0.30 Hz
GB           0
PC                     1.00
```



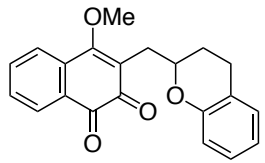
9

^{13}C NMR (150 MHz, acetone-d_6)



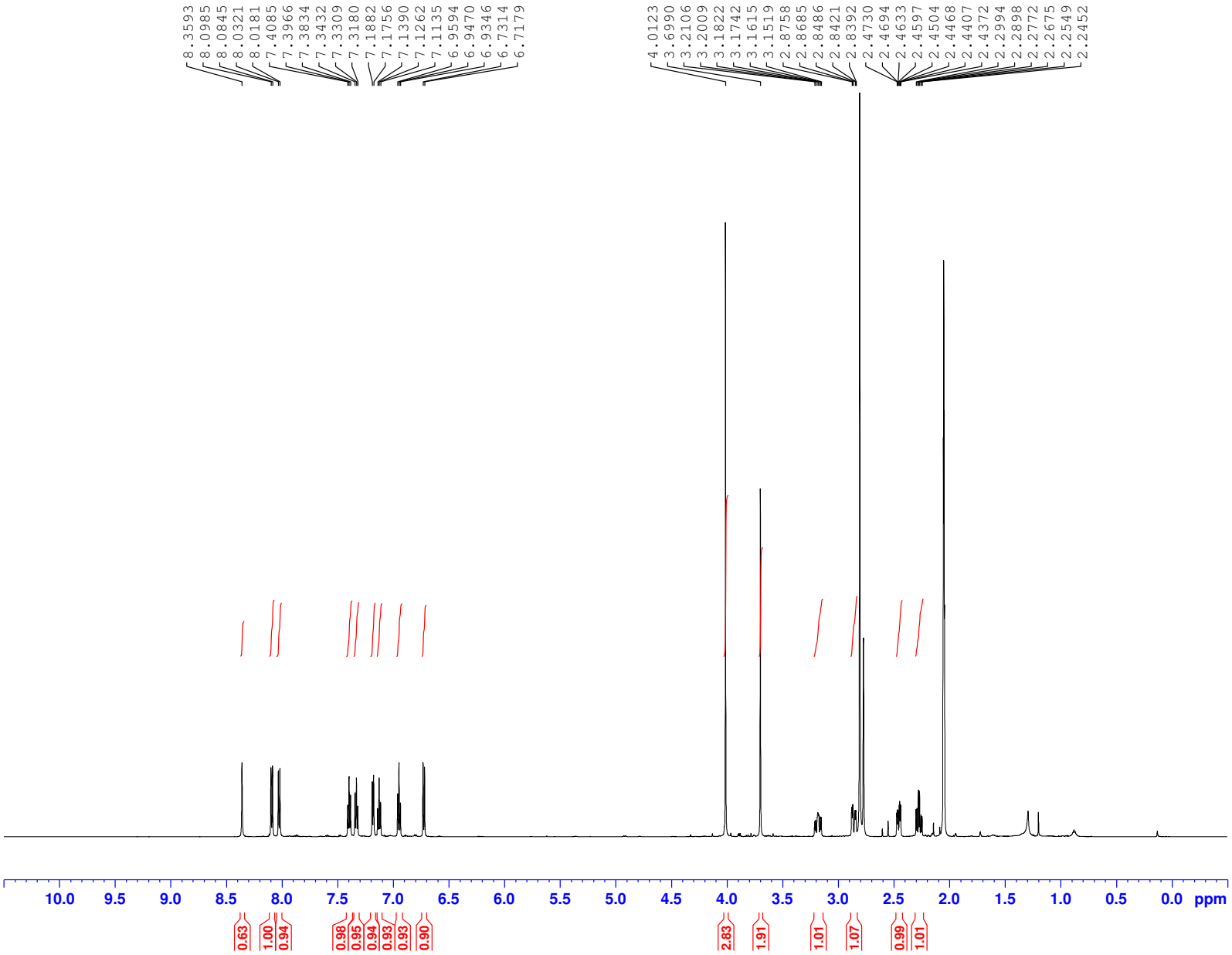



```
Current Data Parameters
NAME                  fw1-308
EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_               20151219
Time                   20.06
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT             Acetone
NS                        512
DS                          4
SWH                36057.691 Hz
FIDRES              0.550197 Hz
AQ                  0.9087659 sec
RG                     175.56
DW                     13.867 usec
DE                     18.00 usec
TE                     300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             150.9178981 MHz
NUC1                     13C
P1                     10.00 usec
PLW1             70.00000000 W

======== CHANNEL f2 ========
SFO2             600.1324005 MHz
NUC2                     1H
CPDPRG[2              waltz16
PCPD2                  70.00 usec
PLW2             26.00000000 W
PLW12             0.76407999 W
PLW13             0.37439999 W

F2 - Processing parameters
SI                       32768
SF               150.9026740 MHz
WDW                         EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

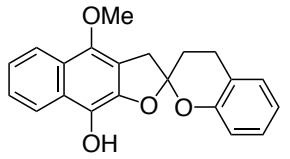


9

^{1}H NMR (600 MHz, acetone-d_6)

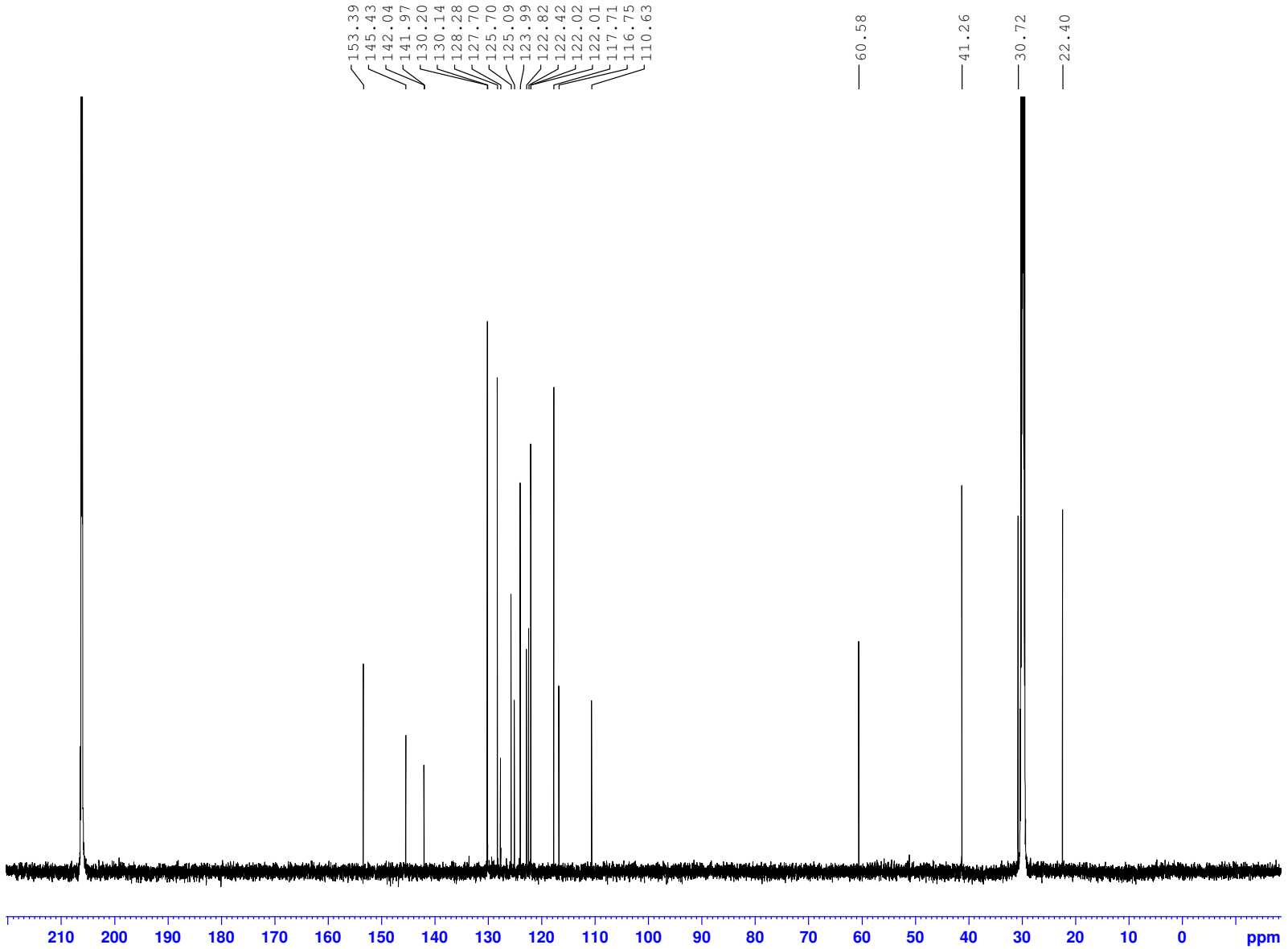



```
Current Data Parameters
NAME                  fw1-300
EXPNO                      22
PROCNO                      1

F2 - Acquisition Parameters
Date_               20151217
Time                    0.07
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG                 zg30
TD                     65536
SOLVENT              Acetic
NS                         64
DS                          2
SWH               12019.230 Hz
FIDRES             0.183399 Hz
AQ                 2.7262976 sec
RG                      31.94
DW                     41.600 usec
DE                     10.00 usec
TE                     300.0 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            600.1337060 MHz
NUC1                       1H
P1                     12.00 usec
PLW1           23.00000000 W

F2 - Processing parameters
SI                     65536
SF              600.1300062 MHz
WDW                       EM
SSB         0
LB                      0.30 Hz
GB          0
PC                      1.00
```

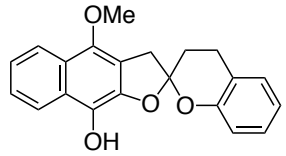


10

^{13}C NMR (150 MHz, acetone-d_6)



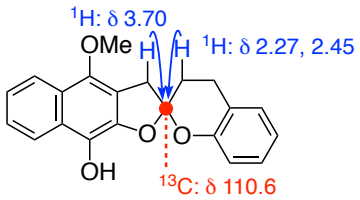

```
Current Data Parameters
NAME                  fw1-300
EXPNO                      23
PROCNO                      1

F2 - Acquisition Parameters
Date_               20151217
Time                    2.41
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG                zgpg30
TD                      65536
SOLVENT                Acetic
NS                        3072
DS                           4
SWH                 36057.691 Hz
FIDRES               0.550197 Hz
AQ                   0.9087659 sec
RG                      175.56
DW                      13.867 usec
DE                      18.00 usec
TE                      300.0 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               150.9178981 MHz
NUC1                       13C
P1                      10.00 usec
PLW1               70.00000000 W

======== CHANNEL f2 ========
SFO2               600.1324005 MHz
NUC2                       1H
CPDPRG[2                waltz16
PCPD2                   70.00 usec
PLW2               26.00000000 W
PLW12               0.76407999 W
PLW13               0.37439999 W

F2 - Processing parameters
SI                        32768
SF                 150.9026707 MHz
WDW                        EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

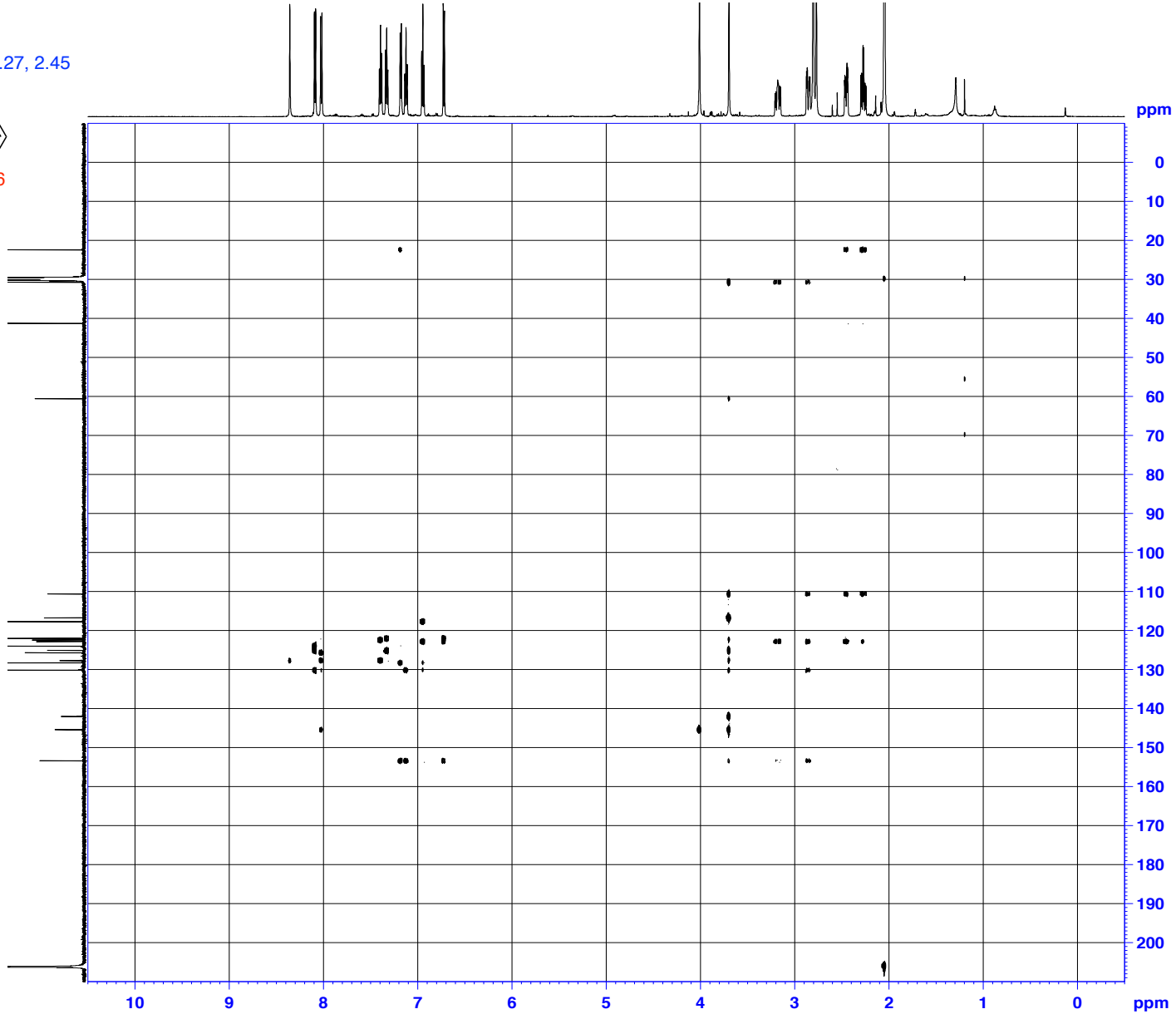


10

HMBC (acetone-d_6)

Key HMBC Correlations





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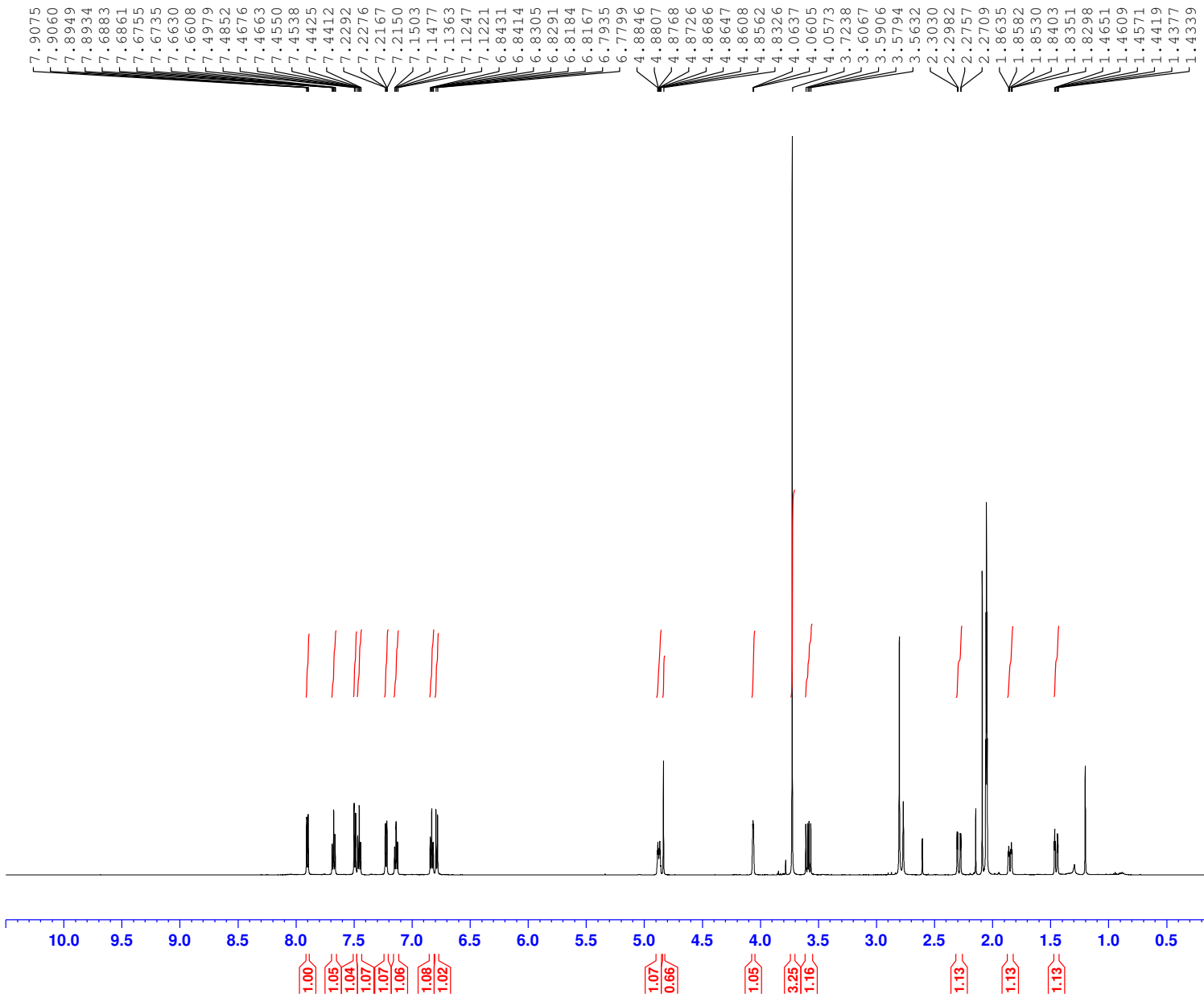
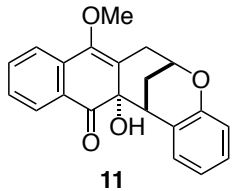
```
Current Data Parameters
NAME                  fw1-300
EXPNO                      26
PROCNO                      1

F2 - Acquisition Parameters
Date_              20151217
Time                   3.27
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG     hmbcetgpl3nd
TD                     4096
SOLVENT             Acetic
NS                        6
DS                       16
SWH               5263.158 Hz
FIDRES            1.284951 Hz
AQ                0.3891200 sec
RG                   175.56
DW                   95.000 usec
DE                   10.00 usec
TE                   300.0 K
CNST6          120.0000000
CNST7          170.0000000
CNST13           8.0000000
CNST30           0.5981153
D0              0.00000300 sec
D1              1.89486897 sec
D6              0.06250000 sec
D16             0.00020000 sec
IN0             0.00001490 sec

======== CHANNEL f1 ========
SFO1           600.1327510 MHz
NUC1                   1H
P1                   12.00 usec
P2                   24.00 usec
PLW1           23.00000000 W

======== CHANNEL f2 ========
SFO2           150.9178734 MHz
NUC2                  13C
P3                   10.00 usec
P24                2000.00 usec
PLW2           70.00000000 W
SPNAM[7]      Crp60comp.4
SPOAL7               0.500
SPOFFS7   0 Hz
SPW7           10.69499969 W

====== GRADIENT CHANNEL =====
GPNAM[1]       SMSQ10.100
GPNAM[3]       SMSQ10.100
GPNAM[4]       SMSQ10.100
GPNAM[5]       SMSQ10.100
GPNAM[6]       SMSQ10.100
GPZ1                80.00 %
GPZ3                14.00 %
GPZ4                -8.00 %
GPZ5                -4.00 %
GPZ6                -2.00 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                     256
SFO1            150.9179 MHz
FIDRES         131.082214 Hz
SW                222.353 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                    2048
SF             600.1300062 MHz
WDW                   SINE
SSB                      4
LB         0 Hz
GB         0
PC                    1.40

F1 - Processing parameters
SI                    1024
MC2          echo-antiecho
SF              150.9026707 MHz
WDW                  QSINE
SSB                      2
LB         0 Hz
GB         0
```

^{1}H NMR (600 MHz, acetone-d_6)

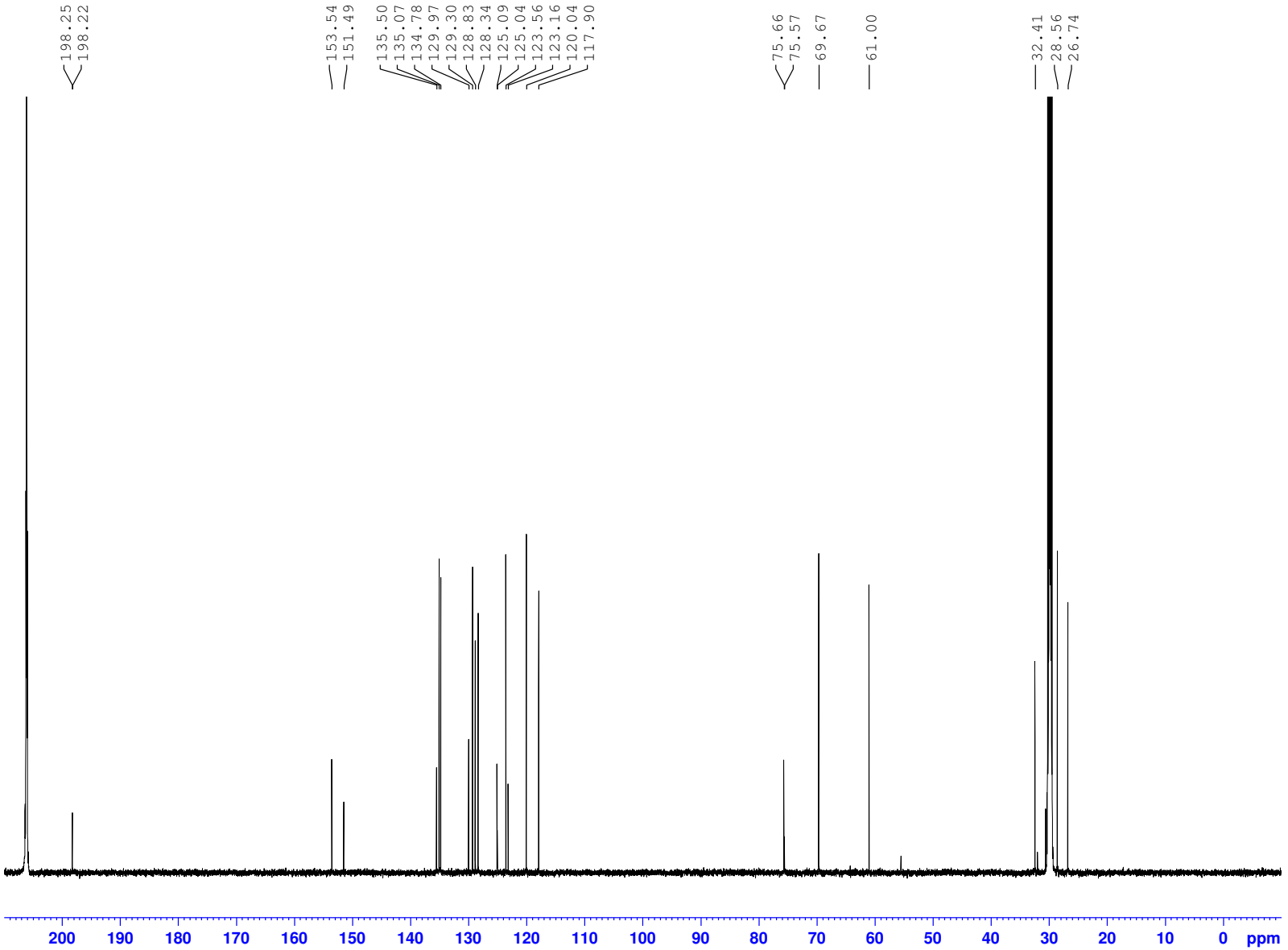



```
Current Data Parameters
NAME                  fw1-318-bp
EXPNO                         30
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20160108
Time                       22.15
INSTRUM                    spect
PROBHD    5 mm CPPBBO BB
PULPROG                    zg30
TD                        65536
SOLVENT                 Acetone
NS                             32
DS                              2
SWH                  12019.230 Hz
FIDRES                0.183399 Hz
AQ                    2.7262976 sec
RG                         31.94
DW                        41.600 use
DE                        10.00 use
TE                        300.0 K
D1                   1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                600.1337060 MHz
NUC1                        1H
P1                       12.00 use
PLW1                23.00000000 W

F2 - Processing parameters
SI                        65536
SF                  600.1300128 MHz
WDW                          EM
SSB                0
LB                        0.30 Hz
GB                 0
PC                        1.00
```

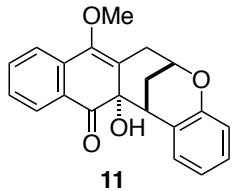


11

^{13}C NMR (150 MHz, acetone-d_6)



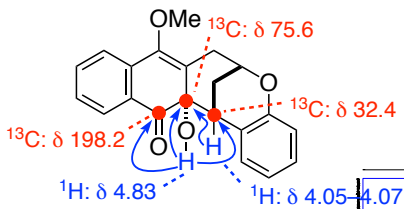

```
Current Data Parameters
NAME          fw1-318-bp
EXPNO                 31
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160109
Time                3.27
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD                 65536
SOLVENT          Acetone
NS                  4096
DS                     4
SWH            36057.691 Hz
FIDRES          0.550197 Hz
AQ             0.9087659 sec
RG                175.56
DW                13.867 use
DE                18.00 use
TE                300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9178981 MHz
NUC1                  13C
P1                  10.00 use
PLW1         70.00000000 W

======== CHANNEL f2 ========
SFO2         600.1324005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2               70.00 use
PLW2         26.00000000 W
PLW12         0.76407999 W
PLW13         0.37439999 W

F2 - Processing parameters
SI                 32768
SF           150.9026724 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

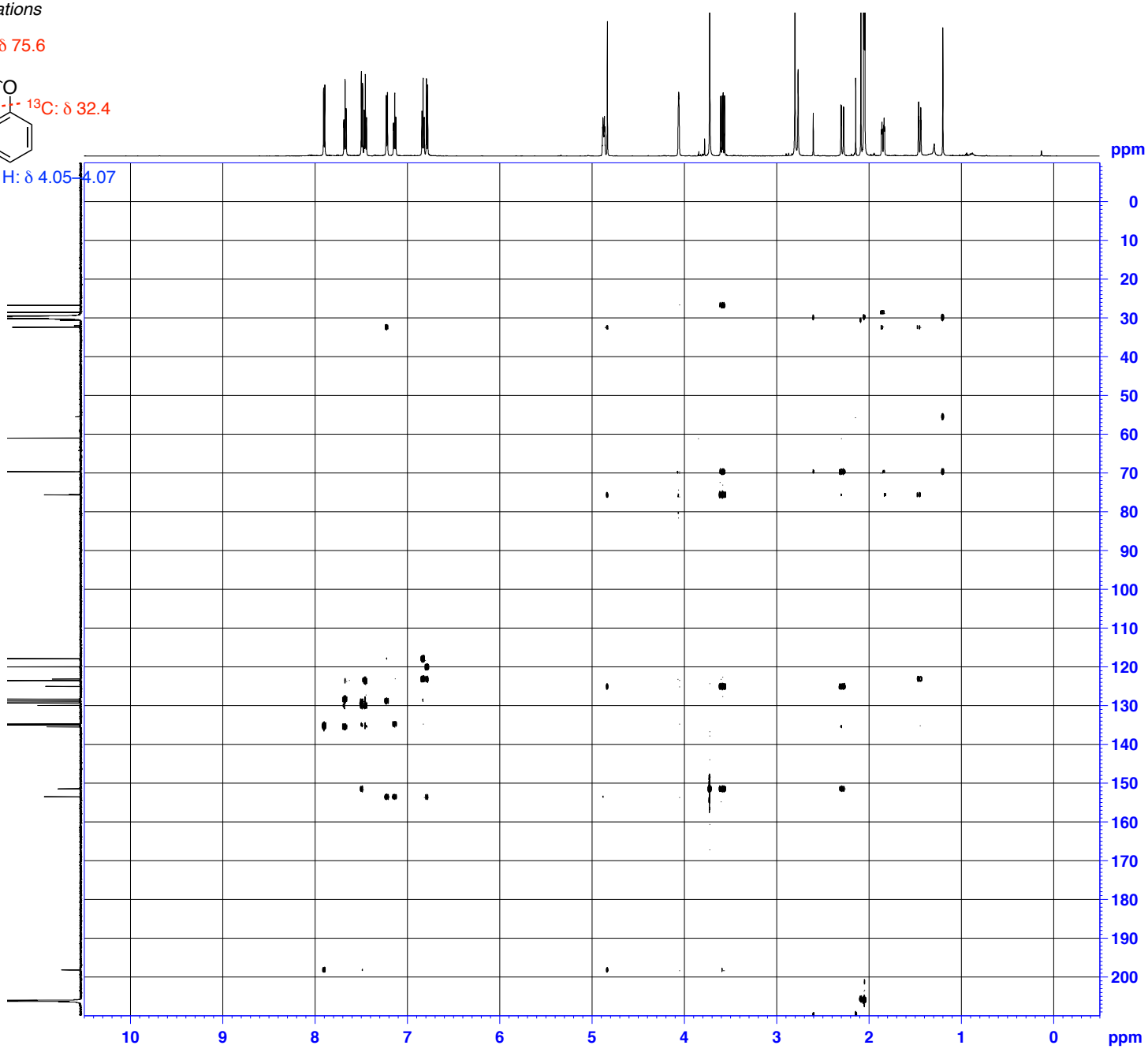


11

HMBC (acetone-d_6)

Key HMBC Correlations





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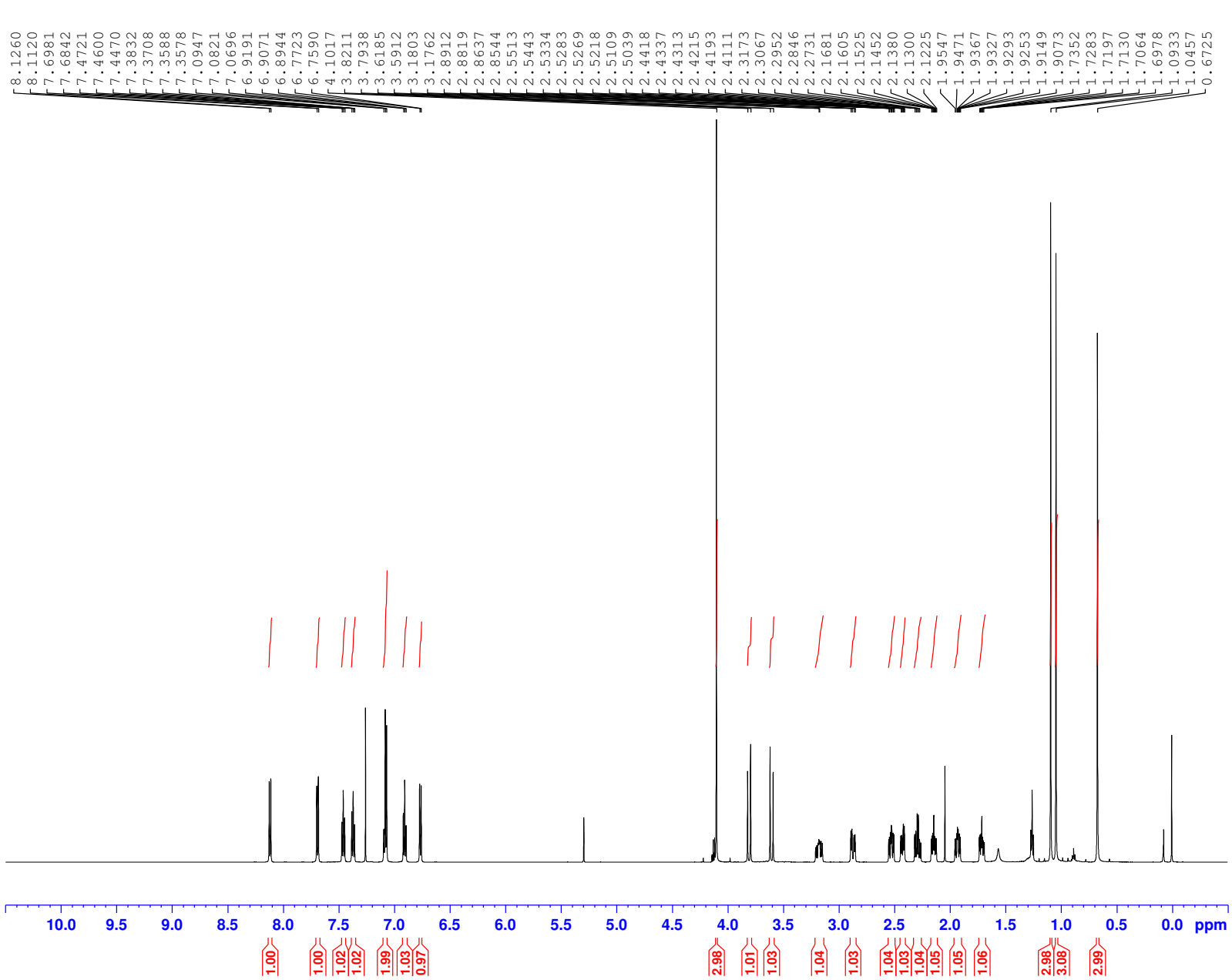
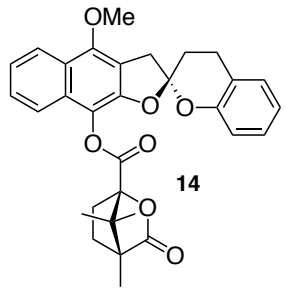
```
Current Data Parameters
NAME          fw1-318-bp
EXPNO                 34
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160109
Time               4.13
INSTRUM           spect
PROBHD   5 mm CPPBBO BB
PULPROG    hmbcetgpl3nd
TD                 4096
SOLVENT         Acetone
NS                    4
DS                   16
SWH           5050.505 Hz
FIDRES        1.233033 Hz
AQ            0.4055040 sec
RG               175.56
DW               99.000 usec
DE               10.00 usec
TE               300.0 K
CNST6        120.0000000
CNST7        170.0000000
CNST13         8.0000000
CNST30         0.5981153
D0           0.00000300 sec
D1           1.87848496 sec
D6           0.06250000 sec
D16          0.00020000 sec
IN0          0.00001490 sec

======== CHANNEL f1 ========
SFO1         600.1326854 MHz
NUC1                 1H
P1                12.00 usec
P2                24.00 usec
PLW1        23.00000000 W

======== CHANNEL f2 ========
SFO2         150.9178734 MHz
NUC2                13C
P3                10.00 usec
P24             2000.00 usec
PLW2        70.00000000 W
SPNAM[7]    Crp60comp.4
SPOAL7            0.500
SPOFFS7  0 Hz
SPW7        10.69499969 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPNAM[4]      SMSQ10.100
GPNAM[5]      SMSQ10.100
GPNAM[6]      SMSQ10.100
GPZ1              80.00 %
GPZ3              14.00 %
GPZ4              -8.00 %
GPZ5              -4.00 %
GPZ6              -2.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                   256
SFO1          150.9179 MHz
FIDRES        131.082214 Hz
SW            222.353 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                  2048
SF           600.1300128 MHz
WDW                 SINE
SSB                    4
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2         echo-antiecho
SF           150.9026724 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
```

^{1}H NMR (600 MHz, $CDCl_3$)




```
Current Data Parameters
NAME                  fw1-1310
EXPNO                       30
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20171119
Time                     18.42
INSTRUM                  spect
PROBHD    5 mm CPPBBO BB
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 12019.230 Hz
FIDRES                0.183399 Hz
AQ                    2.7262976 sec
RG                         17.5
DW                       41.600 use
DE                       10.00 use
TE                       300.0 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1                600.1337060 MHz
NUC1                        1H
P1                       12.00 use
PLW1                23.00000000 W

F2 - Processing parameters
SI                      65536
SF                  600.1300145 MHz
WDW                        EM
SSB                 0
LB                        0.30 Hz
GB                  0
PC                        1.00
```



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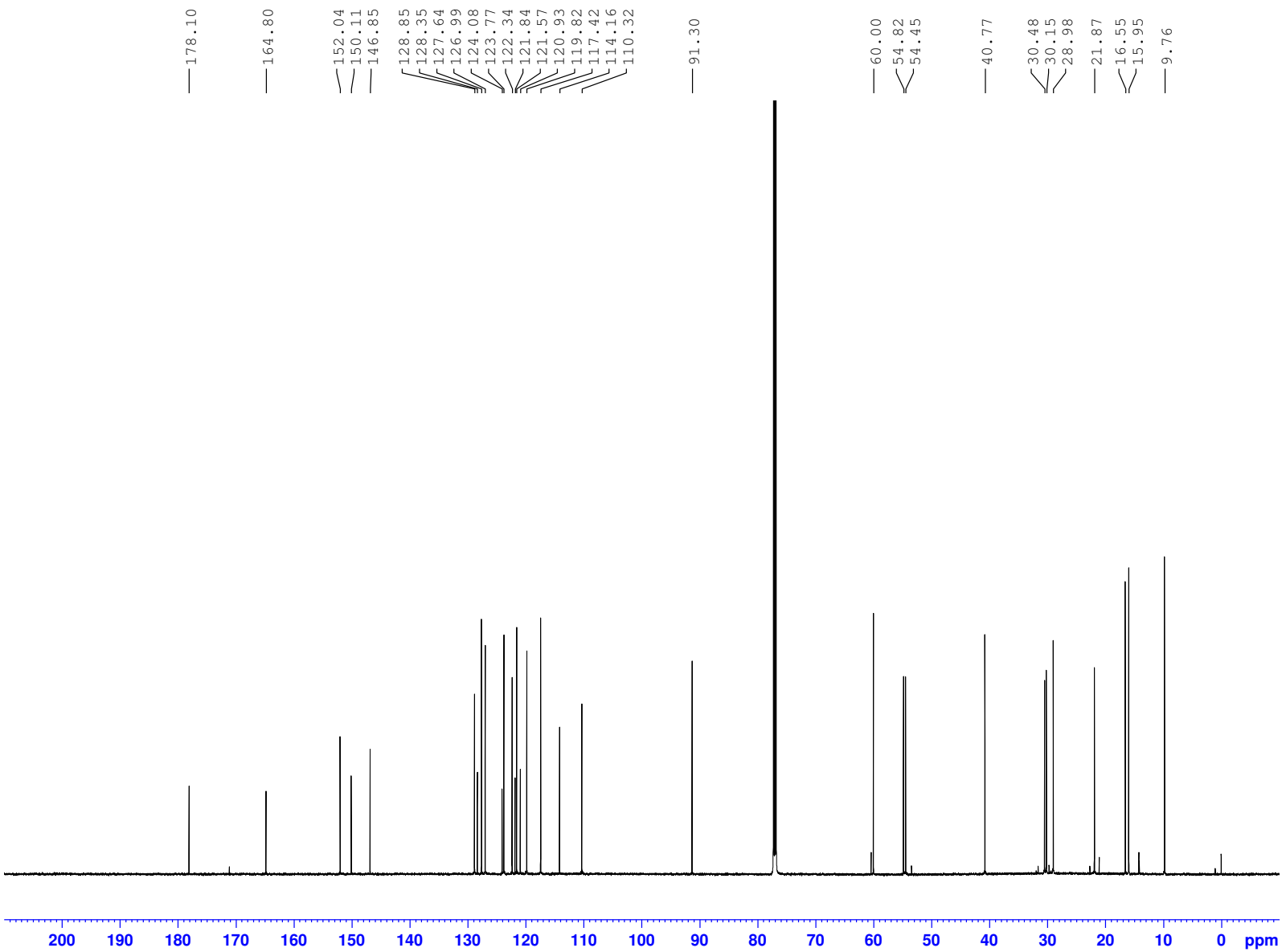
^{13}C NMR (150 MHz, $CDCl_3$)



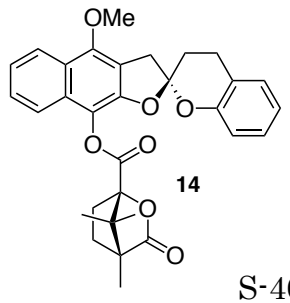

```
Current Data Parameters
NAME                  fw1-1310
EXPNO                       31
PROCNO                       1

F2 - Acquisition Parameters
Date_              20171120
Time                    4.59
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       2048
DS                          4
SWH                36057.691 Hz
FIDRES              0.550197 Hz
AQ                  0.9087659 sec
RG                     175.56
DW                     13.867 usec
DE                      18.00 usec
TE                     300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             150.9178981 MHz
NUC1                     13C
P1                     10.00 usec
PLW1            70.00000000 W

======== CHANNEL f2 ========
SFO2             600.1324005 MHz
NUC2                     1H
CPDPRG[2              waltz16
PCPD2                  70.00 usec
PLW2            14.00000000 W
PLW12            0.64286000 W
PLW13            0.32335001 W

F2 - Processing parameters
SI                       32768
SF               150.9028102 MHz
WDW                         EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```



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